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STUDY OF FACTORS AFFECTING REACTIONS IN ENVIRONMENTAL CHAMBERS

Raphael J. Jaffe

Lockheed Missiles and Space Company

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Environmental Protection Agency

20 May 1972

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PB 212 715

STUDY OF

FACTORS AFFECTING REACTIONS IN ENVIRONMENTAL CHAMBERS

FINAL REPORT ON PHASE I

by Raphael J. Jaffe

Contract CAPA 1-69 (1-71)
Prepared for the
COORDINATING RESEARCH COUNCIL
New York, N.Y.

and

Contract 68-02-0038
Prepared for the
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

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An environmental chamber was designed and fabricated for use in a study of factors affecting reactions in environmental chambers. The chamber is illuminated with a collimated beach of light from a solar illumination simulator consisting of a zenon arc lamp and optical system, to facilitate subsequent studies in which various surface materials and surface/volume ratios will be used, and the incident radiation will be varied in spectrum, intensity, and time behavior. The environmental chamber is constructed of Pyrex glass and Teflon coated aluminum extrusions, and sealed with silicone rubber. It is 66 ft^3 volume and has an S/V of 1.43 ft^{-1}. This report describes the facilities; the analytical chemistry methodology; the characteristics of the chamber and illuminator; the photochemical experiments; and gives conclusions and recommendations.

17. Key Words and Document Analysis. 17a. Descriptors

Irradiation Chamber
Manifold
Nitrogen Dioxide
Nitric Oxide
Ozone
Propylene
Carbon Monoxide
Formaldehyde
Acetaldehyde
Hydrocarbons
Air Pollution
Photolysis

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New York, New York

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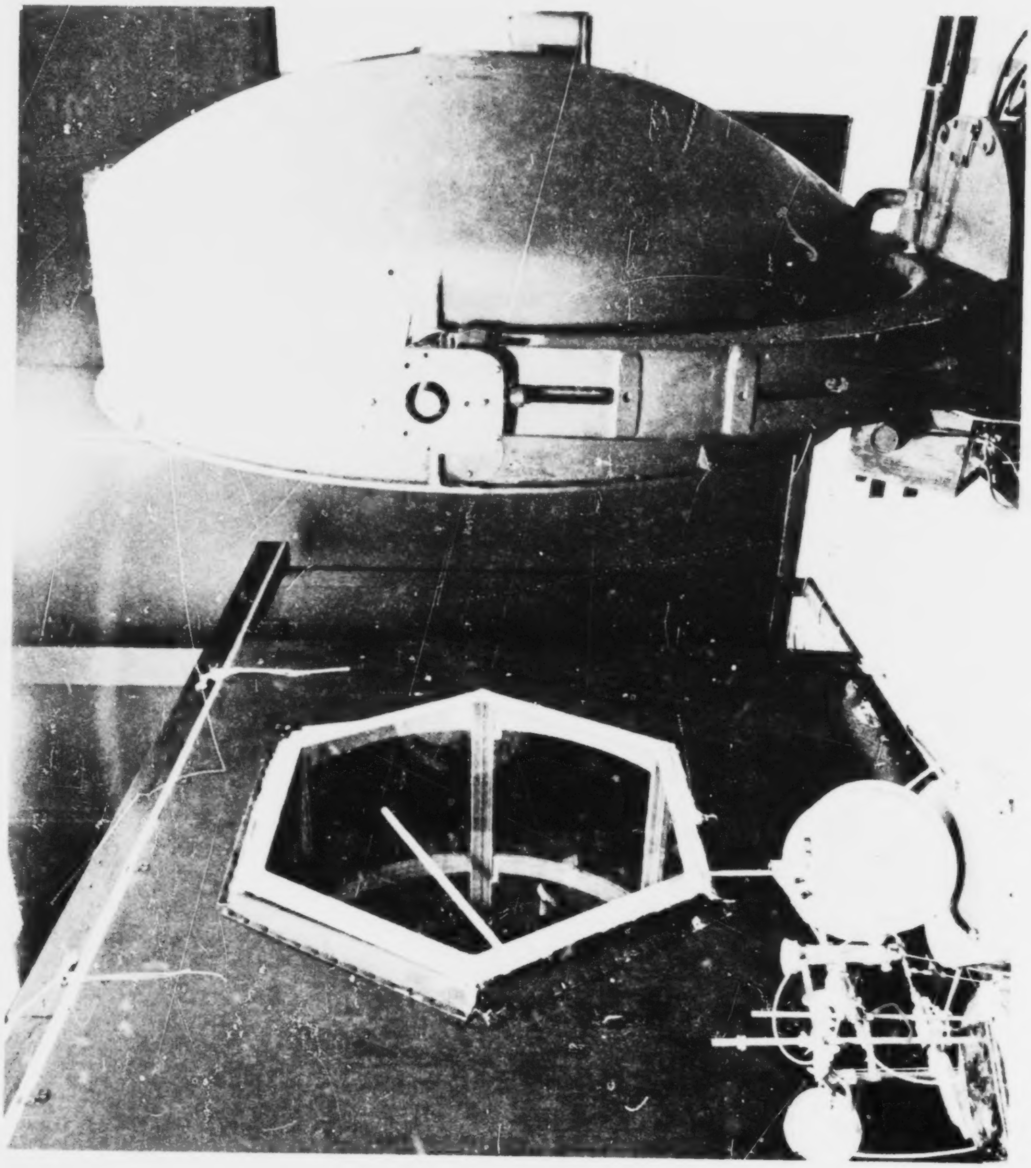
BIOTECHNOLOGY ORGANIZATION
LOCKHEED MISSILES & SPACE COMPANY



Environmental Chamber Inside Thermal Enclosure, with Solar Simulator in Position

SUMMARY

An environmental chamber was designed and fabricated for use in a study of factors affecting reactions in environmental chambers. The chamber is illuminated with a collimated beam of light from a solar illumination simulator consisting of a xenon arc lamp and optical system, to facilitate subsequent studies in which various surface materials and surface/volume ratios will be used, and the incident radiation will be varied in spectrum, intensity, and time behavior. The environmental chamber is constructed of Pyrex glass and Teflon coated aluminum extrusions, and sealed with silicone rubber. It is 66 ft^3 volume and has an S/V of 1.43 ft^{-1}.

The following chamber characteristics were determined: leakage rate of 0.4% per hour, NO_2 absorption of 0.4% per hour; and ozone halflife of 10.6 hours (in the dark at 75°F) and 3.5 hours (in the light at 95°F). Photolysis of NO_2 shows a K_d of 0.35 per minute.

Three replicate photochemical runs with the propylene/NO_x system (3 ppm/1.5 ppm) were conducted. The following average values were determined: NO_2 formation rate - 15 ppb/min, time to NO_2 maximum - 82 minutes, NO_2 dosage - 160 ppm-minutes; Maximum oxidant concentration - 0.56 ppm; time to oxidant maximum - 130 minutes, oxidant dosage - 88 ppm-minutes; and time to destroy half of the initial propylene - 98 minutes.

These calculated values for the reaction manifestations are within the range of values reported by the Coordinating Research Council CAPI-6 group for the same reactant system photochemically reacted in the various environmental chambers. For example, the half-time for hydrocarbon disappearance ranges from 60 to 180 minutes for the various chambers, compared to 98 minutes for the subject chamber. This indicates that the subject chamber will be useful in the future experimental program, in that the starting configuration gives results similar to those previously obtained.

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1. INTRODUCTION

Chambers in which systematic studies can be made of the reactions between hydrocarbons and nitrogen oxide in the presence of simulated sunlight have been in use for some twenty years. Such chambers have generally been successful in simulating the features of photochemical smog, such as production of oxidants and eye irritants, and haze. Intensive comparisons of results obtained in eleven such chambers have been performed by the Coordinating Research Council project CAPA-6-69, Techniques for Irradiation Chamber Studies. The range of physical characteristics of these chambers is shown in Table 1-1. A group of round-robin tests were conducted using these chambers: (1) irradiation of seven different hydrocarbons with nitrogen oxide; (2) replicate runs to establish reproducibility using the propylene-nitrogen oxide system; (3) a reactant concentration study in which 3 ppm propylene was reacted with 3, 1.5, and 0.5 ppm nitrogen oxides (Ref. 1-1).

Project CAPA-1-69, Factors Affecting Reactions in Environmental Chambers, has been established by the Coordinating Research Council as part of the activities of the Air Pollution Research Advisory Committee's efforts, which is a jointly sponsored Industry (Automobile Manufacturers Association and American Petroleum Institute) - Government (Environmental Protection Agency) activity. The objective of CAPA-1-69 is to study how various design and operational variables affect the reactions which occur in environmental chambers.

The report covers work performed under contract by the Biotechnology Organization of Lockheed Missiles and Space Company, under the guidance of the CAPA-1-69 project group. The objective of this work is to design, fabricate, and establish repeatability of an irradiation chamber that:

1) is capable of accommodating varying areas of diverse surface materials such as glass, Teflon-type polymers, aluminum and stainless steel;
2) can be irradiated using varying mean radiation intensity, intensity-time relationships, and spectral distribution; and
3) can be reproducibly cleaned for complete decontamination.

The chamber and illuminator are designed to facilitate a program to establish important factors affecting irradiation chamber reactions. The CAPA-1-69 project group has advanced seven hypotheses to account for the difference among chambers. These hypotheses say that differences among chambers are due to:

TABLE 1-1

CHARACTERISTICS OF CHAMBERS USED FOR PREVIOUS INTERCOMPARISON INVESTIGATIONS

Volume (ft^3)	2.9 to 1140
Surface/Volume Ratio (ft^{-1})	0.78 to 4.91
Surface Type as S/V	
Stainless Steel	0 to 2.44
Aluminum	0 to 0.92
Glass	0 to 2.81
Plastic Film	0 to 0.83
Light Intensity (K_d, min.$^{-1}$)	0.16 to 0.40

1) variations in surface-volume ratios
2) variations in surface materials
3) variations in surface cleanliness
4) variations in radiation intensities
5) variations in intensity-time distribution of the radiation
6) variations in spectral distribution
7) interaction of surface variables with reactant concentrations and chamber conditions.

This report describes the facilities (Section 2); the analytical chemistry methodology (Section 3); the characteristics of the chamber and illuminator (Section 4); the photochemical experiments (Section 5); and gives conclusions and recommendations (Section 6).

2. FACILITY DESCRIPTION

The facilities developed for the experimental activities planned for this program are described in the following sections. These facilities include (1) a Pyrex irradiation chamber in which the photochemical reactions take place, (2) a xenon-arc illuminator to provide visible and ultraviolet energy for the reactions, (3) a thermal enclosure to maintain the irradiation chamber gas temperature at the desired level during a photochemical run, (4) a charging system to charge the irradiation chamber with reactants, (5) sample manifolds, (6) a vacuum chamber cleaning system to clean the chamber between photochemical runs, (7) gas analysis equipment to monitor the reaction products during a photochemical run, and (8) photometric equipment to monitor the intensity and spectral characteristics of the solar illuminator.

2.1 Irradiation Chamber

The irradiation chamber is hexagonal in cross-section measuring 54 inches across the diagonal of the cross section. The chamber configuration is shown in Figure 2-1 and the chamber support stand is shown in Figure 2-2. Figure 2-3 presents a pictoral view of the chamber. The chamber is constructed of six flat side panels that fit into an extruded aluminum framework. The aluminum framework is coated with 5-8 mils of FEP Teflon. The resultant panels are bolted together and are supported from circular rings on the stand.

The faces of the chamber are of tempered 1/4" Pyrex glass to admit the light and pass the beam through the chamber with minimal reflection or absorption. The flat sides of the chamber are also fabricated from 1/4" tempered Pyrex glass. The working stress of the tempered Pyrex is 3600 psi, which results in an allowable pressure differential of 7.1 inches of water. This is based on the hexagonal faces which are the weakest members. Sealing of the 1/4" Pyrex to the aluminum extrustions is accomplished with silicon rubber gaskets that have been off-gassed at about 10^{-5} torr for over 24 hours. The gasket is fitted between the aluminum channel and the Pyrex, and the Pyrex is pressed into a channel section in the extrusion. A silicon rubber O-ring is used to seal adjacent aluminum extrusions which are bolted together. Additional sealing is accomplished with a coat of Dow Corning 30-121 RTV silicon rubber on all external joints.

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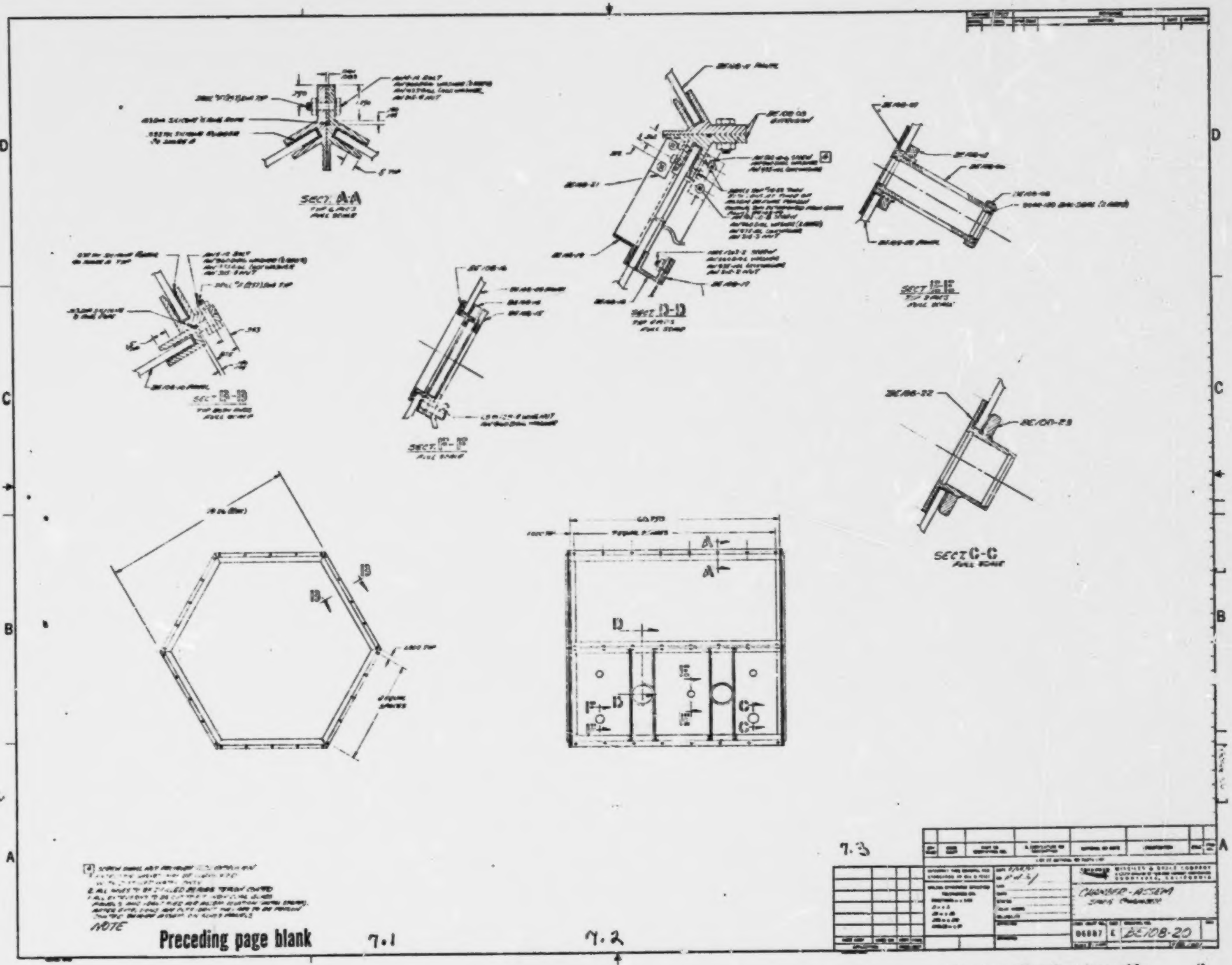
SECT. A-A
SECT. B-B
SECT. F-F
SECT. D-D
SECT. E-E
SECT. C-C
FULL SCALE
NOTE
CHAMBER - ASSEM
BE108-20
D
C
B
A

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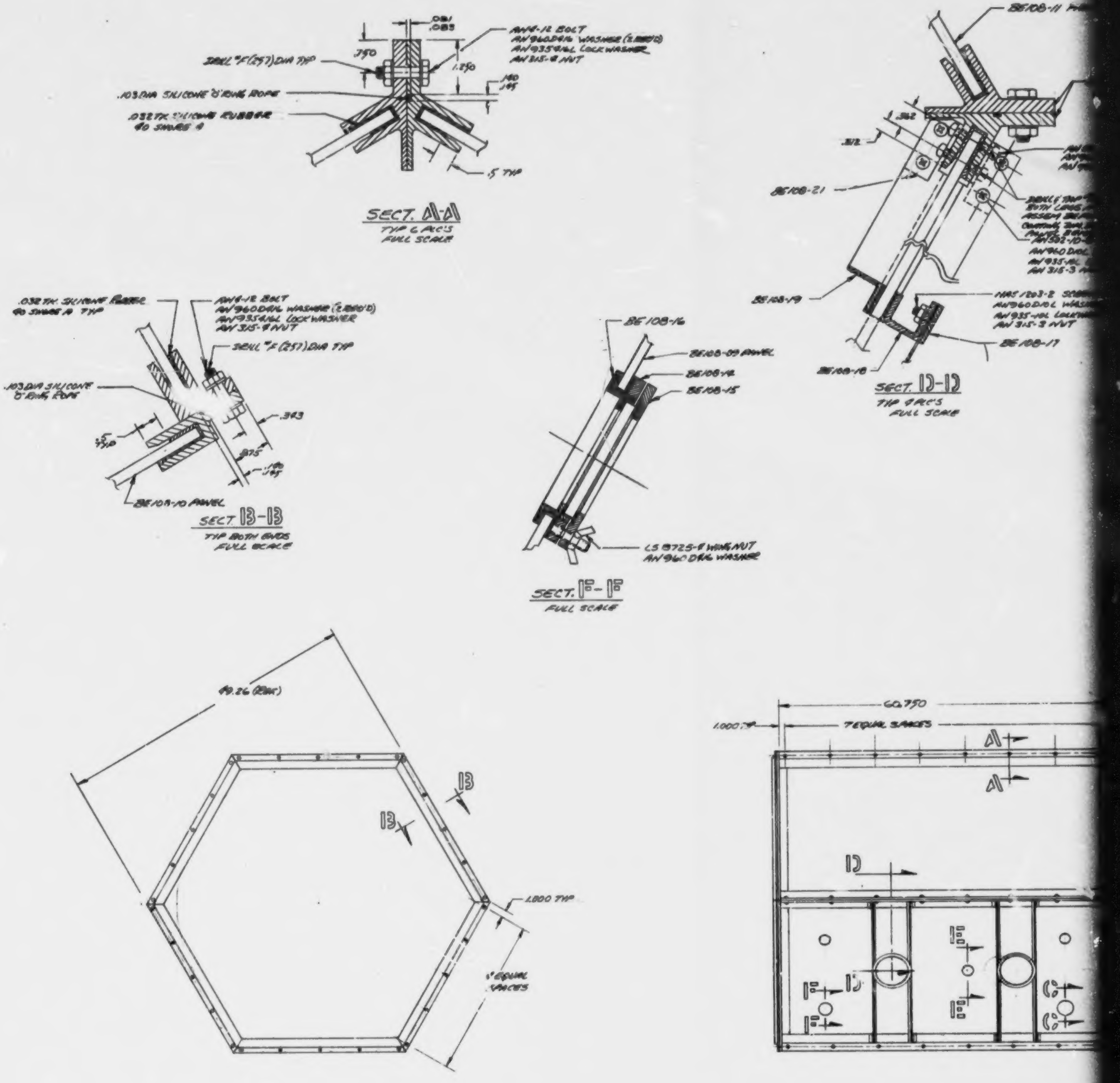
7.1

7.2

7.3

see the following pages for greater detail.

Fig. 2-1 Chamber Assembly


.081
.085
.750
DRILL "F"(257) DIA TYP
1.250
AN4-12 BOLT
AN960D416 WASHER (2 REQ'D)
AN935416L LOCKWASHER
AN315-4 NUT
.140
.145
.103 DIA SILICONE 'O' RING ROPE
.032 TK SILICONE RUBBER
40 SHORE A
.5 TYP
SECT. A-A
TYP 6 PLC'S
FULL SCALE
.032 TK. SILICONE RUBBER
40 SHORE A TYP
AN4-12 BOLT
AN960D416 WASHER (2 REQ'D)
AN935416L LOCKWASHER
AN315-4 NUT
DRILL "F" (257) DIA TYP
.103 DIA SILICONE
'O' RING ROPE
.5 TYP
.343
.875
.140
.145
BE108-10 PANEL
SECT. B-B
TYP BOTH ENDS
FULL SCALE
BE108-16
BE108-09 PANEL
BE108-12
BE108-15
LS 8725-4 WING NUT
AN960 D416 WASHER
SECT. F-F
FULL SCALE
BE108-11
.312
.312
BE108-21
BE108-19
BE108-18
AN315-3 NUT
MS 1203-2
AN960D10L
AN935-10L
AN 315-3 NUT
BE108-17
SECT. D-D
TYP 4 PLC'S
FULL SCALE
49.26 (REF)
B
B
1.000 TYP
EQUAL SPACES
60.750
1.000 TYP
7 EQUAL SPACES
A
A
D
F
F
D
F
F
G
G

4 SCREW SHALL NOT PROTRUDE THRU EXTRUSION
3 EXTRUSION GASKET MAY BE LUBRICATED WITH DISTILLED WATER ONLY
2. ALL HOLES TO BE DRILLED BEFORE TEFLON COATED
1. ALL EXTRUSIONS TO BE CUT TO FIT INDIVIDUAL GLASS PANELS AND IDENTIFIED FOR ASSEM. LOCATION (METAL STAMP). AFTER EXTRUSIONS ARE CUT & IDENT. THEY ARE TO BE TEFLON COATED BEFORE ASSEM. ON GLASS PANELS

NOTE

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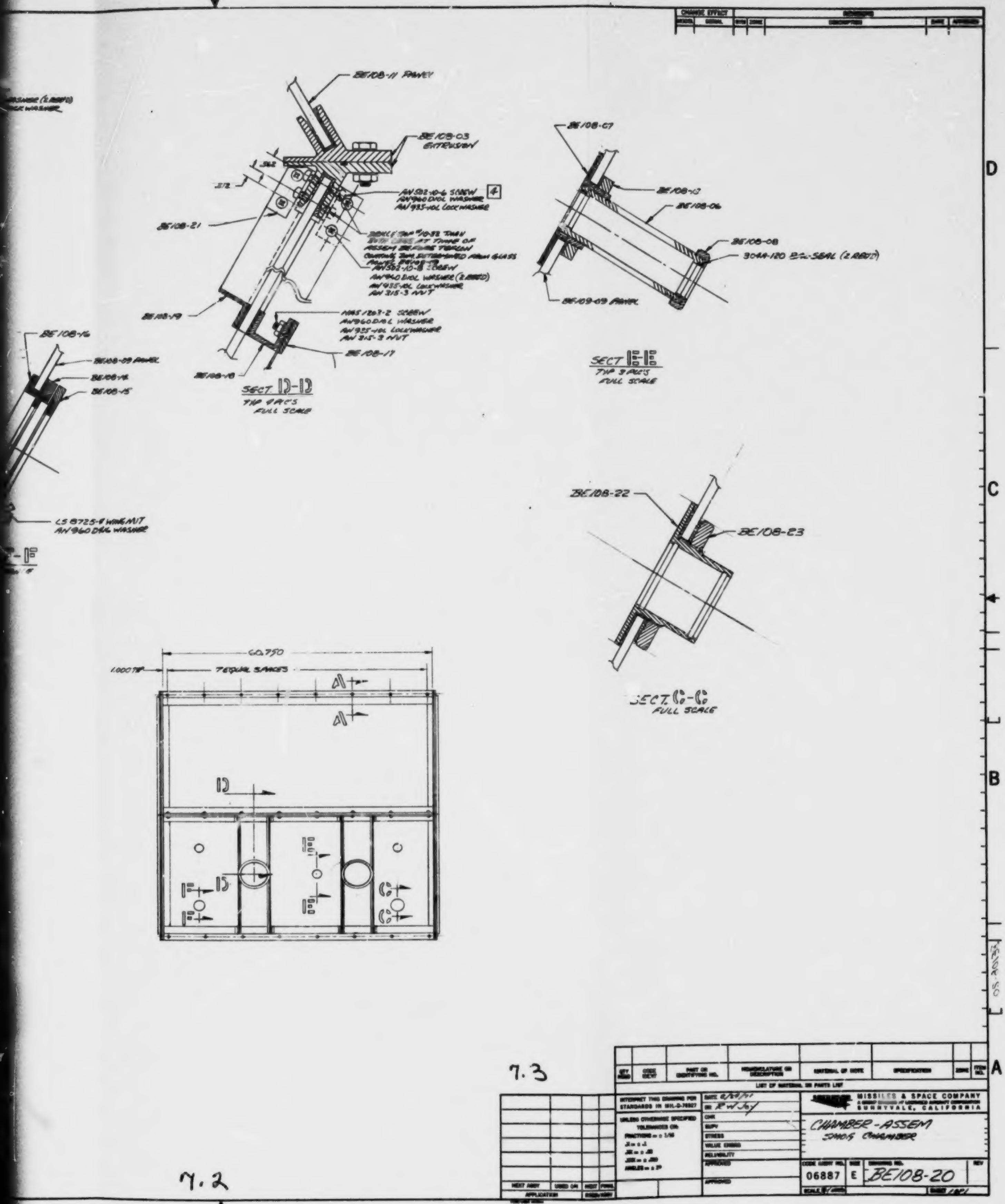
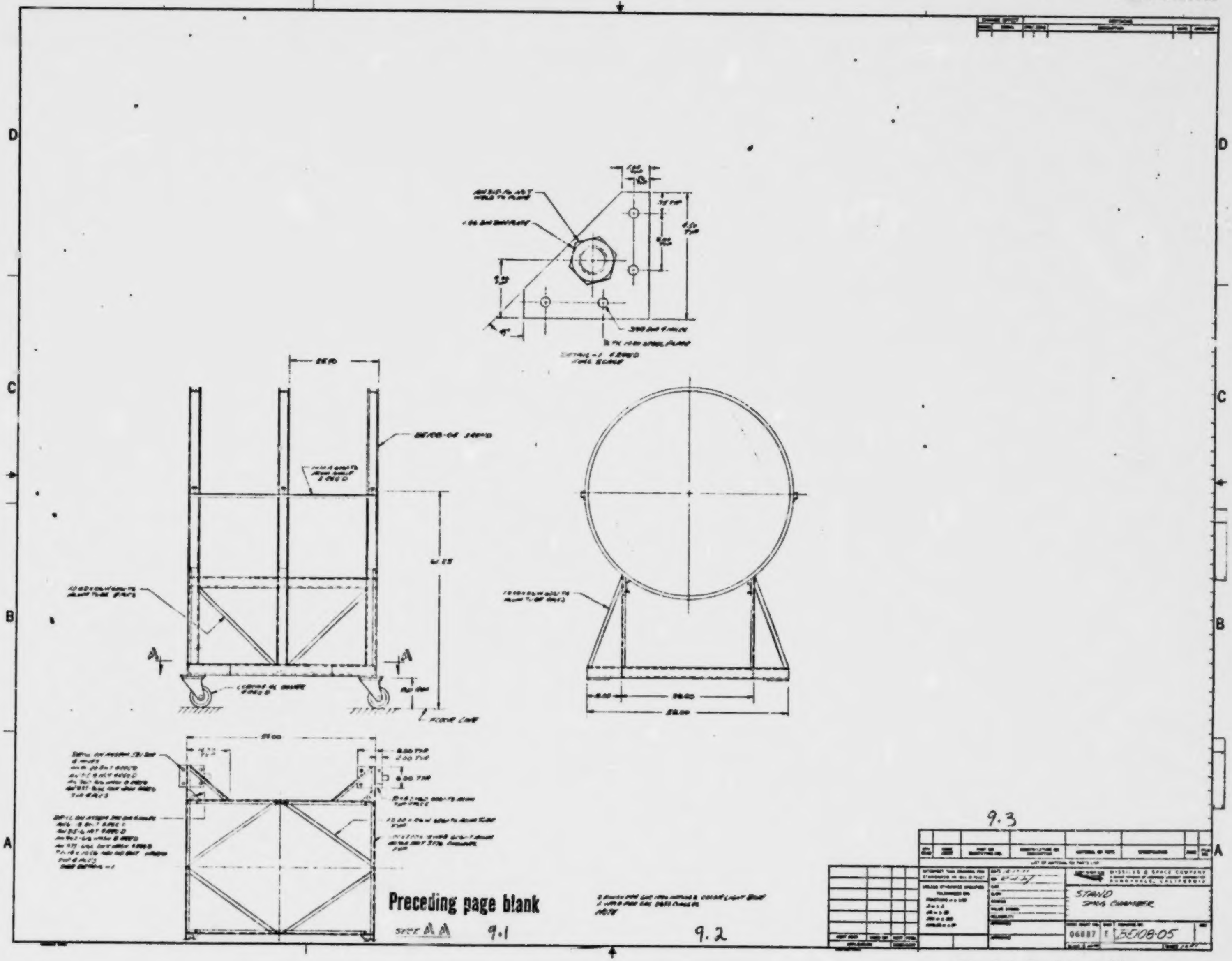

BE108-11 PANEL
BE108-03 EXTRUSION
.562
.372
AN502-10-6 SCREW
AN960D10L WASHER
AN935-10L LOCK WASHER
4
BE108-21
DRILL & TAP #10-32 THRU BOTH LEGS AT TIME OF ASSEM BEFORE TEFLON COATING. TRIM EXTERNAL FROM GLASS PANEL BE108-19
AN502-10-8 SCREW
AN960D10L WASHER (2 REQD)
AN935-10L LOCKWASHER
AN315-3 NUT
BE108-19
NAS1203-2 SCREW
AN960D10L WASHER
AN935-10L LOCKWASHER
AN315-3 NUT
BE108-17
BE108-18
SECT D-D
TYP 4 PLC'S
FULL SCALE
WASHER (2 REQD)
LOCK WASHER
BE108-16
BE108-09 PANEL
BE108-14
BE108-15
LS 8725-8 WING NUT
AN960D8L WASHER
BE108-07
BE108-13
BE108-06
BE108-08
3044-120 BAL-SEAL (2 REQD)
BE109-09 PANEL
SECT E-E
TYP 3 PLC'S
FULL SCALE
BE108-22
BE108-23
SECT. C-C
FULL SCALE
60.750
1.000 TYP
7 EQUAL SPACES
A
D
E
C
D
C
B
A
7.3
7.2
LIST OF MATERIAL OR PARTS LIST
MISSILES & SPACE COMPANY
SUNNYVALE, CALIFORNIA
CHAMBER-ASSEM
SMDS CHAMBER
06887
E
BE108-20
R W Joy

Fig. 2-1 Chamber Assembly


D
C
B
A
A
A
SECT A-A
MISSILES & SPACE COMPANY
SUNNYVALE, CALIFORNIA
STAND
SPACE CHAMBER
06887
E
3E108-05

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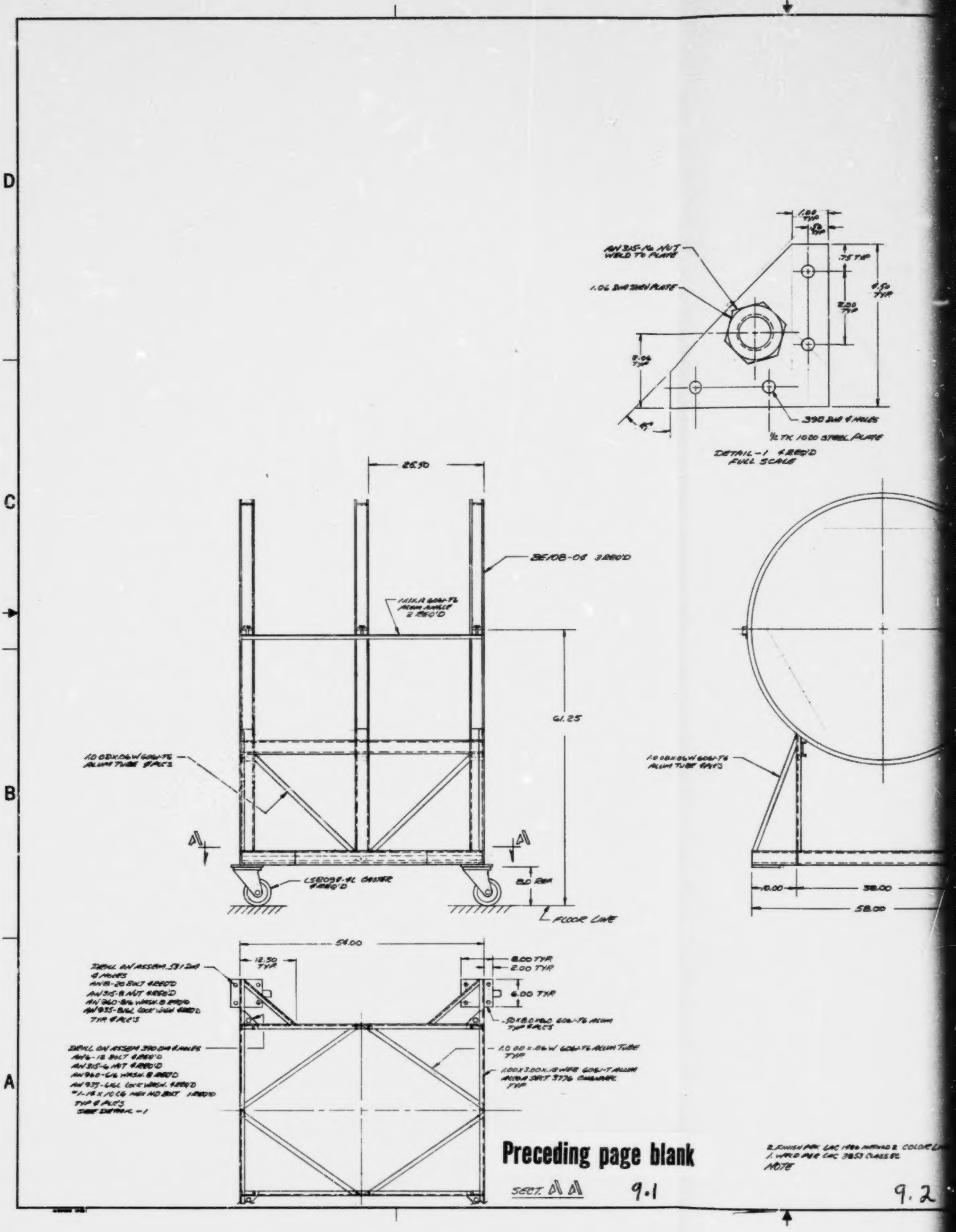
9.1

9.2

9.3

See the following pages for greater detail.

Fig. 2-2 Stand Assembly


D
C
B
A
AN 315-16 NUT WELD TO PLATE
1.06 DIA THRU PLATE
1.00 TYP
.75 TYP
4.50 TYP
2.00 TYP
2.06 TYP
45°
.390 DIA 4 HOLES
½ TK 1020 STEEL PLATE
DETAIL-1 4 REQ'D FULL SCALE
26.50
BE108-04 3 REQ'D
1X1X.12 6061-T6 ALUM ANGLE 2 REQ'D
61.25
1.0 OD X .06 W 6061-T6 ALUM TUBE 4 PC'S
A
A
LS8098-4L CASTER 4 REQ'D
8.0 REF
FLOOR LINE
54.00
12.50 TYP
8.00 TYP
2.00 TYP
6.00 TYP
DRILL ON ASSEM .531 DIA 4 HOLES
AN8-20 BOLT 4 REQ'D
AN315-8 NUT 4 REQ'D
AN960-816 WASH. 8 REQ'D
AN935-816 LOCK WASH 4 REQ'D
TYP 4 PLC'S
.50 X 8.0 X 6.0 6061-T6 ALUM TYP 4 PLC'S
DRILL ON ASSEM .390 DIA 4 HOLES
AN6-12 BOLT 4 REQ'D
AN315-6 NUT 4 REQ'D
AN960-616 WASH. 8 REQ'D
AN935-616 LOCK WASH. 4 REQ'D
*1-14 X 10.06 HEX HD BOLT 1 REQ'D
TYP 4 PLC'S
SEE DETAIL -1
1.0 OD X .06 W 6061-T6 ALUM TUBE TYP
1.00 X 3.00 X .18 WEB 6061-T ALUM ALCOA SECT 3776 CHANNEL TYP
SECT. A A
1.0 OD X .06 W 6061-T6 ALUM TUBE 4 PC'S
10.00
38.00
58.00
2. FINISH PER LAC 1986 METHOD 2 COLOR
1. WELD PER LAC 3853 CLASS 3C
NOTE

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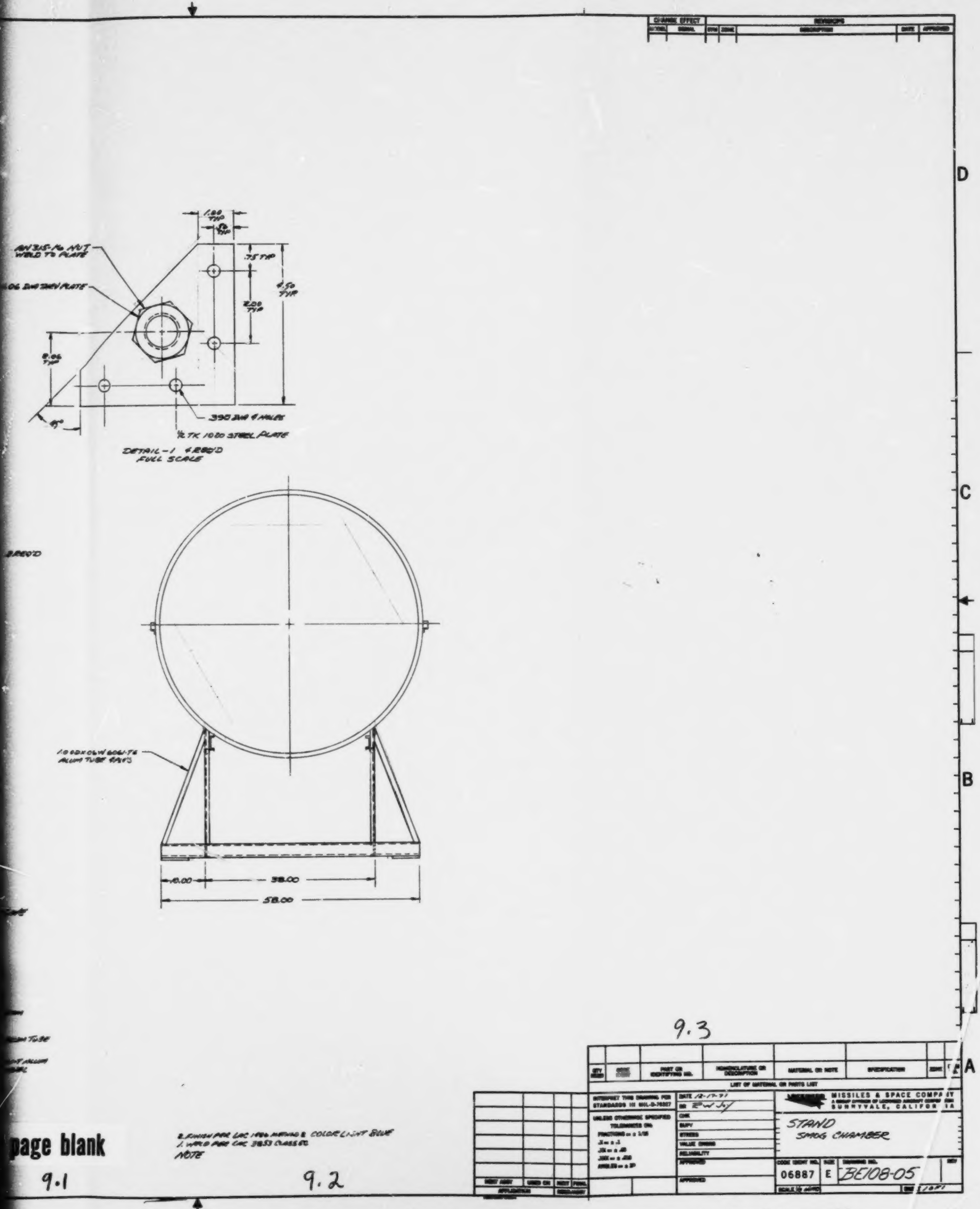
9.1

9.2


AN 315-16 NUT WELD TO PLATE
.06 DIA THRU PLATE
1.00 TYP
.50 TYP
.75 TYP
2.00 TYP
4.50 TYP
2.06 TYP
45°
.390 DIA 4 HOLES
½ TK 1020 STEEL PLATE
DETAIL-1 4 REQ'D
FULL SCALE
REQ'D
1.00 OD X .06 W 6061-T6 ALUM TUBE 4 REQ'S
10.00
38.00
58.00
D
C
B
A
CHANGE EFFECT
REVISIONS
DESCRIPTION
DATE
APPROVED
QTY REQD
PART OR IDENTIFYING NO.
NOMENCLATURE OR DESCRIPTION
MATERIAL OR NOTE
SPECIFICATION
ZONE
LIST OF MATERIAL OR PARTS LIST
INTERPRET THIS DRAWING PER STANDARDS IN MIL-D-70327
UNLESS OTHERWISE SPECIFIED TOLERANCES ON:
DATE 12-17-71
DR
CHK
SUPV
STRESS
VALUE ENGRG
RELIABILITY
APPROVED
MISSILES & SPACE COMPANY
SUNNYVALE, CALIFORNIA
STAND
SMOG CHAMBER
CODE IDENT NO. 06887
SIZE E
DRAWING NO. BE108-05
SCALE
NEXT ASSY
USED ON
APPLICATION

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2. FINISH PER LAC 1986 METHOD 2, COLOR LIGHT BLUE
1. WELD PER LAC 3853 CLASS C
NOTE

9.1

9.2

9.3

Fig. 2-2 Stand Assembly

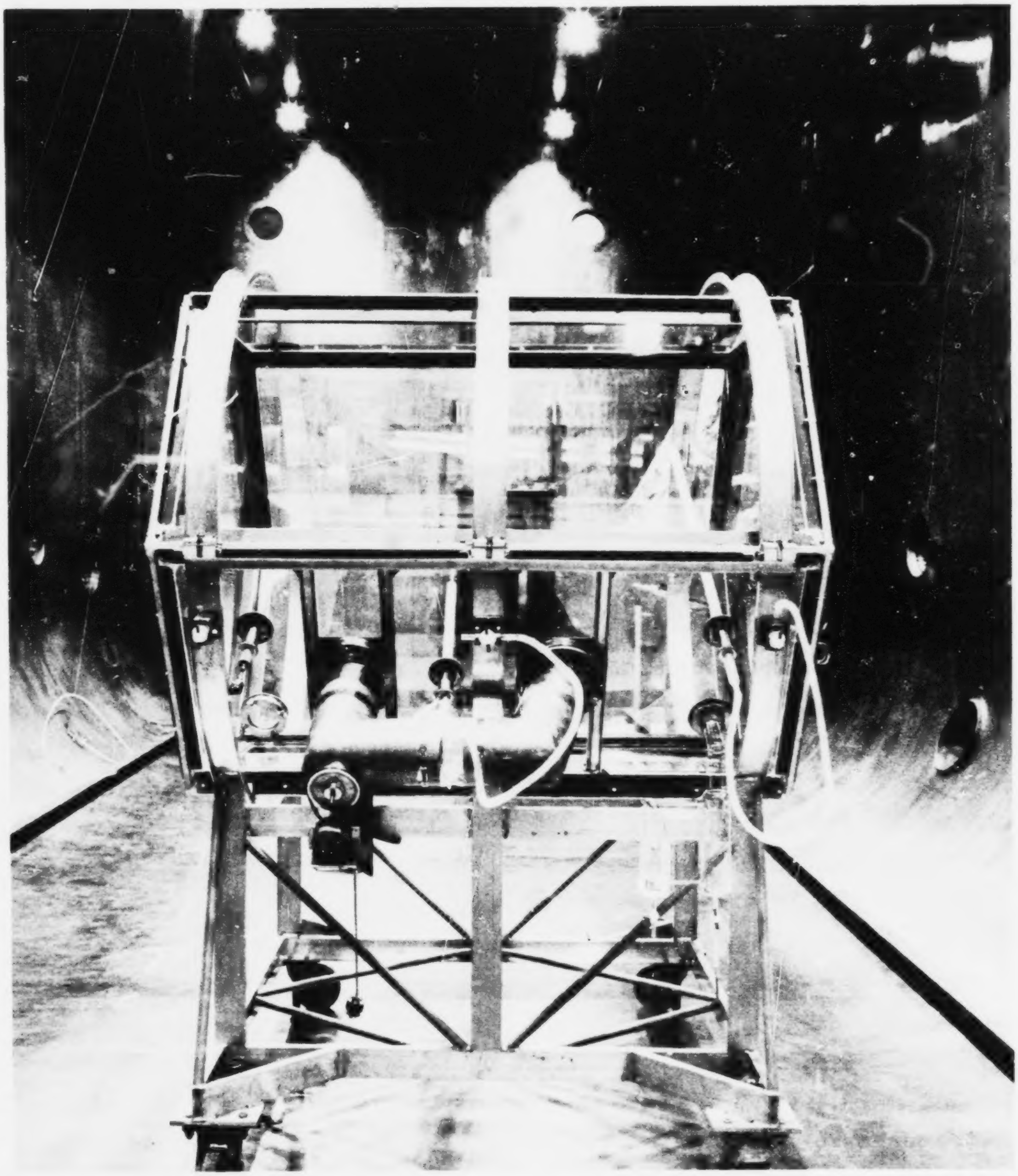

Fig. 2-3 Environmental Chamber Showing Side Stream Mixer, Charge Ports, and Clean-Out Port

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Three 1-inch diameter ports are located in one of the lower side panels. The ports are fabricated from brass and are coated with FEP Teflon. Sealing of these ports to the Pyrex chamber walls is accomplished with silicon rubber gaskets. Sealing of tubes inserted into the ports is accomplished with Teflon seals. Tubes can be fitted into these ports and adjusted to various distances into the hexagon. The rear port is used for a gas thermocouple, which is Teflon coated and shielded from direct illuminator radiation. The center port is used for gas sampling. A 1" diameter pyrex tube containing a concentric 7 millimeter diameter tube is used for gas withdrawal. The grab samples are withdrawn from the 1" diameter tube while the continuous flow samples are taken from the 7 millimeter diameter tube. The smaller diameter tube is used for the continuous flow samples to minimize sample residence time. The front port has a 1" diameter Pyrex tube installed that is used for make up air addition.

A cleanout port is located in this same Pyrex panel. This port is 3" in diameter and is used for chamber outgassing during chamber cleaning. A Pyrex disc with a silicon rubber gasket is used to seal this port during normal operation. Metallic parts are all coated with FEP Teflon. A Pyrex relief valve is also mounted on this panel. This relief valve has a 2 inch diameter opening leading to the chamber. The valve utilizes a water seal principle and the relief setting is adjusted by the addition or withdrawal of water. Both negative and positive differential pressure protection is provided. An overflow trap is included to prevent water from entering the chamber.

A side stream mixer is also located on this panel. This mixer consists of a 6-inch diameter duct connected to the panel at a point 1/3 of the way from the front and 1/3 of the way from the rear of the chamber. Gas is circulated through the duct by means of a Teflon-coated fan blade installed in the duct. The blade is connected to a shaft that penetrates the duct through a rotary Teflon seal. The shaft is connected to a motor via a pulley and belt which are all located outside of the chamber. The fan is rotated at 250 rpm producing a circulation rate of approximately 75 cfm. The inlet end of the duct enters the chamber at a 45° angle to minimize short circuiting of the gas circulation. All parts in the side stream recirculator are coated with Teflon. The mixer is only operated prior to a photochemical experimental run.

The chamber is mounted at each hexagonal apex to a circular structural framework, which in turn mounts to a dolly with casters for easy transport of the chamber. The structural frame is configured to allow chamber assembly within the framework. A locating jack system is used to adjust the height of the chamber to exactly match the height of the light source.

Geometric characteristics of the chamber are summarized in Table 2-1.

Table 2-1
Chamber Description

Configuration:	Hexagonal prism
Length:	60 inches
Diagonal:	54 inches
Volume:	65.9 ft^3
Surface Area:	
End Plates	26.4 ft^2
Side Plates	67.5 ft^2
Total	93.9 ft^2
S/V	1.43 ft^{-1}

2.2 Illuminator

The irradiation source for the chamber is external to the chamber. This external source consists of an arc lamp situated in front of a large parabolic reflector. Collimated energy from the reflector is directed toward the chamber. The collimated beam used as the light source for the irradiation chamber is 5 feet in diameter. The light source for the illumination system is an air cooled Osram compact xenon arc lamp (6,500 watt nominal rating). The fireball for the lamp is 2.4 by 9 mm. The optical system consists of a 5 ft. diameter parabolic primary mirror and a spherical back collector mirror. The primary mirror is made of copper with a rhodium plating with aluminum over the rhodium. An SiO_x protective coating is on top of the aluminum. This produces a reflectance of approximately 0.8 at a wave length of 300 millimicrons. The spherical back reflector is rhodium coated which would produce a reflectance of approximately 0.7 at the same wave length. (Ref. 2-1). The back reflector is utilized to capture energy from the lamp that would normally not strike the parabola, and focus it back on the parabolic reflector. The optical system collects about 35% of the lamp radiated light and directs it as a collimated beam into the chamber front face.

The illuminator is integrated into a search light housing. The housing is on casters which allows the illuminator to be moved readily.

2.3 Thermal Enclosure

A thermal enclosure is used to control the chamber temperature during a photochemical run. Design requirements for the thermal enclosure are maintenance of chamber gas temperature at 95 ± 3°F. The enclosure, depicted pictorally in Figure 2-4 with the chamber installed, consists of a plywood housing insulated with fiberglass with heated air circulating throughout the enclosure. The enclosure has a hexagonal shaped hole in the rear to allow one end of the irradiation chamber to protrude. This allows energy passing through the chamber to be transmitted outside of the thermal enclosure. The front end of the thermal enclosure has sliding doors that allow easy removal and installation of the chamber. These doors also have a hexagonal shaped hole that will allow the forward end of the irradiation chamber to protrude out. This allows the illuminator energy to enter the chamber. Both the rear and forward hexagonal openings in the enclosure fit tightly to the chamber to minimize gas leakage from the enclosure. The interior surfaces of the enclosure are insulated with 3 inches of fiberglass.

A centrifugal blower is utilized to circulate approximately 1500 cfm of air over four 1.3 kw heaters that are used for thermal control. Three of the heaters are manually switched on or off and the fourth heater is thermostatically controlled to maintain the enclosure air temperature at a fixed level. This system allows use of the fixed heaters for warm up and coarse temperature control with fine temperature control being accomplished with the thermostatically controlled heater. The thermal sensor is a mercury thermometer with an integral switching circuit, set for 95 ± 0.2°F. This controls the air temperature in the thermal enclosure. Air circulation is accomplished with a centrifugal blower that passes air through plenums located at the bottom of the thermal enclosure. The heaters are located in these plenums. Air passes out of the plenums, over the chamber and is withdrawn out of the top of the thermal enclosure, where it is recirculated to the heater plenum. The thermal enclosure is approximately 8' high by 8' wide by 6' long.

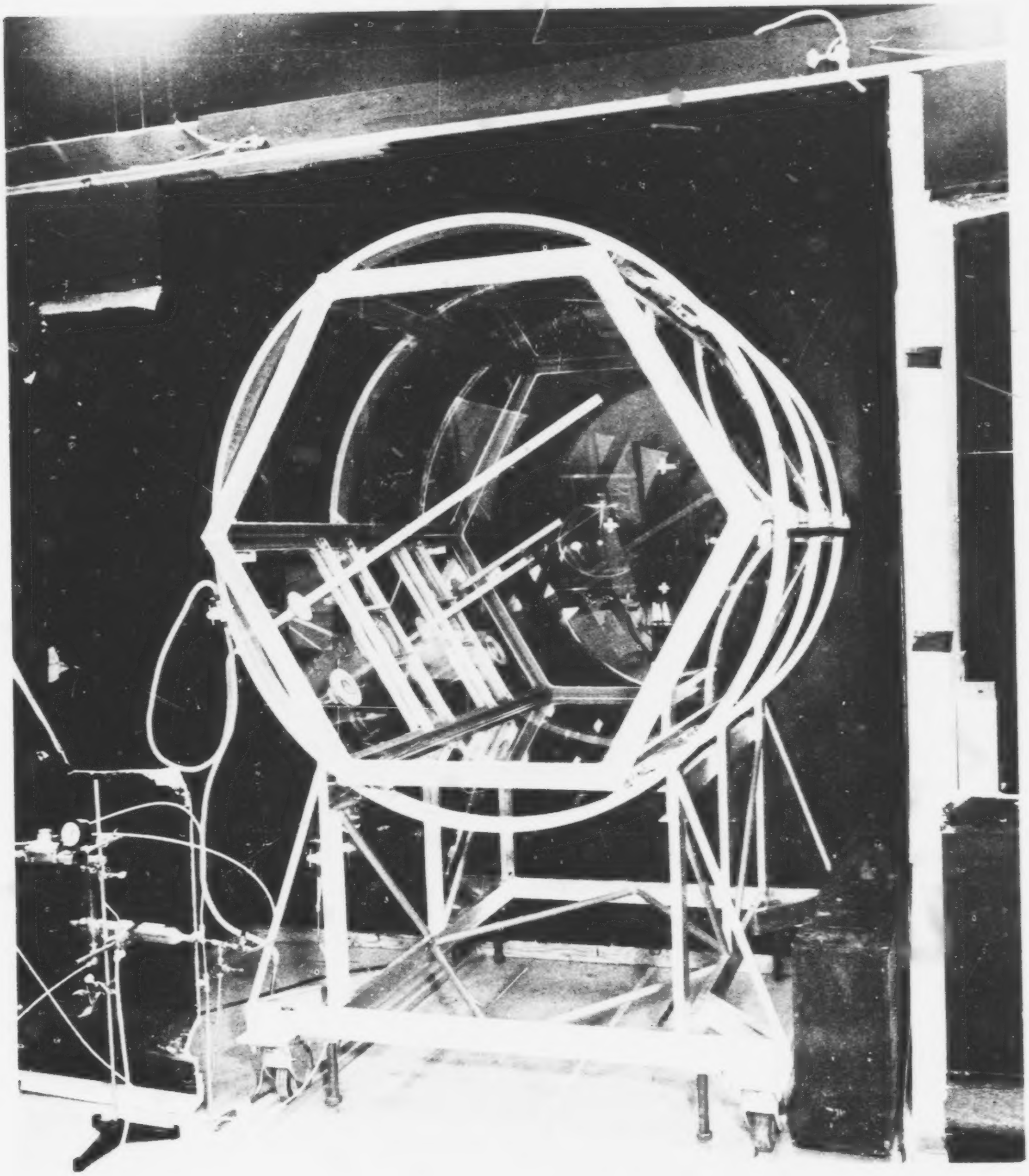

Fig. 2-4 Chamber Inside Thermal Enclosure

2.4 Charging System

Charging systems are provided for the purposes of (1) chamber recompression following a vacuum cleaning, (2) reactant charging prior to a photochemical run, and (3) make up air to replace chamber leakage and sample withdrawal during a photochemical run. These three charging systems are depicted in Figures 2-5 through 2-7, and are described below. The charging system used for chamber recompression consists of a cylinder of ultra zero air, a flow control valve, flow meter, and humidifier.

Ultra zero air used in the chamber was purchased from Liquid Carbonics, Inc., San Carlos, Cal. It is produced from oxygen made by water electrolysis which is then put through a catalytic oxidizer to reduce the hydrogen content, and from liquid nitrogen. The certified analysis of the ultra zero air is less than 0.1 ppm total hydrocarbons and less than 1 ppm hydrogen. Hydrocarbon content was verified independently by Lockheed by comparison to a methane standard (see Section 3).

Flow control is accomplished by visually monitoring a flow indicator mounted to the irradiation chamber cleanout port and maintaining a positive out flow while the vacuum chamber is being repressurized. The humidifier consists of a stainless steel canister filled with 1 inch Beryl saddles and 2-1/2 gallons of distilled water. The Beryl saddles are provided to obtain uniform gas flow distribution throughout the water. By operating the humidifier at ambient temperature, a dew point slightly in excess of the desired dew point is obtained. Final dew point adjustment is made by the addition of ultra zero air through the make up air system.

The reactant charging system is utilized to charge the reactants, nitric oxide and propylene, into the chamber. The system consists of a cylinder of ultra zero nitrogen, a flow control valve, flow meter, and 500 cc pressure cylinders of 700 ppm nitric oxide in ultra zero nitrogen and 1400 ppm propylene in ultra zero nitrogen.

To minimize initial conversion of NO to NO_2, the nitric oxide is introduced into the side stream mixer with a nitrogen purge stream. In this way, the concentration of nitric oxide is reduced as quickly as possible, which makes the conversion $2NO + O_2 \rightarrow 2NO_2$ very slow. The amount of nitrogen added is small and does not significantly alter the chamber oxygen concentration.

Fig. 2-5 Irradiation Chamber Recompression System

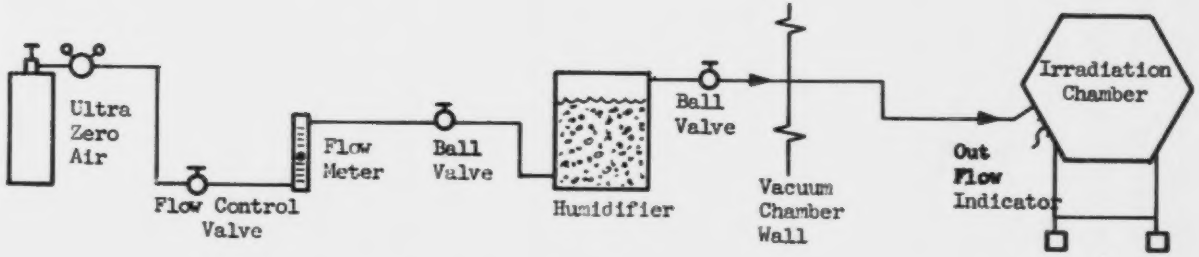
Ultra
Zero
Air
Flow Control
Valve
Flow
Meter
Ball
Valve
Humidifier
Ball
Valve
Vacuum
Chamber
Wall
Out
Flow
Indicator
Irradiation
Chamber

Fig. 2-5

Fig. 2-6 Reactant Charging System

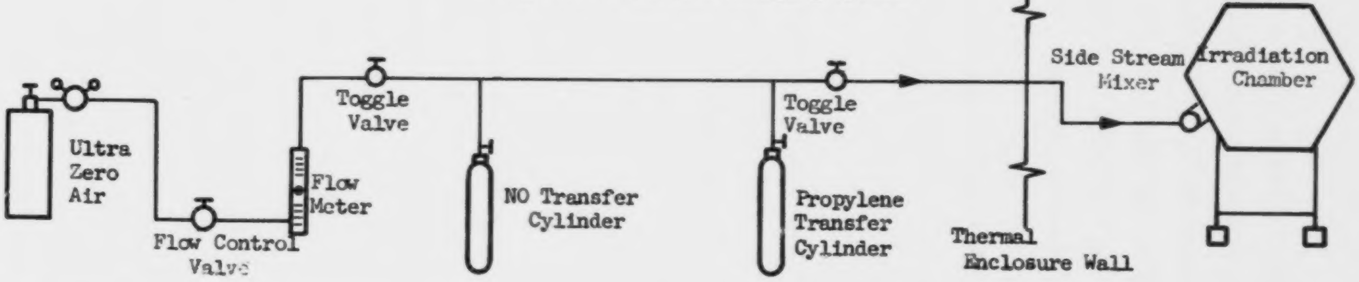
Ultra
Zero
Air
Flow Control
Valve
Flow
Meter
Toggle
Valve
NO Transfer
Cylinder
Toggle
Valve
Propylene
Transfer
Cylinder
Thermal
Enclosure Wall
Side Stream
Mixer
Irradiation
Chamber

Fig. 2-6

Fig. 2-7 Make Up Air System

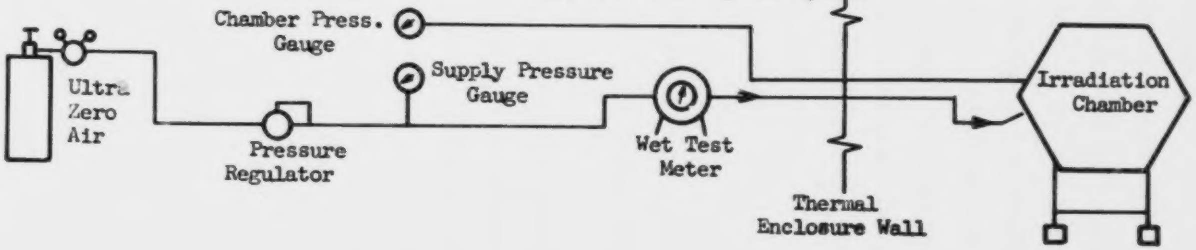
Ultra
Zero
Air
Pressure
Regulator
Chamber Press.
Gauge
Supply Pressure
Gauge
Wet Test
Meter
Thermal
Enclosure Wall
Irradiation
Chamber

Fig. 2-7

Propylene addition is done directly from a 500 cc cylinder with a short nitrogen purge following the propylene introduction.

The makeup air system is utilized to provide and monitor makeup air that is required to replace the air lost due to gas sampling and chamber leakage. The makeup air system consists of a cylinder of ultra zero air, a pressure regulator which controls chamber pressure, a supply pressure gauge, a wet test meter, and a chamber pressure gauge. The wet test meter is used to monitor the total quantity of makeup air used during an experimental run. A positive pressure of approximately 0.1 inches of water is maintained during the run by the pressure regulator.

2.5 Sample Manifolds

Two manifolds were used to sample the chamber. The smaller three outlet manifold used for the NO_2, NO_x and oxidant monitoring, has a volume of 60 cc, while the sampling line from the chamber to the manifold has a 20 cc volume. A total flow rate of 450 cc/min of gas through the manifold provides for a lag time from the chamber to the instrument inlets of about 18 seconds.

The larger 7-outlet manifold, having a 735 cc total volume including the sampling line from the chamber, is used to obtain samples for the other analyses. The dew point apparatus is attached at the farthest outlet from the chamber. The next outlet has a rubber septum for direct syringe sampling. The third outlet is used for bubbler samples for formaldehyde-potassium iodide oxidant measurements. The next two outlets are blank, as is the outlet closest to the chamber. The second outlet from the end, closest to the chamber, was used for grab samples. A flow through either the dew point instrument or a bubbler was established to insure a representative grab sample.

2.6 Cleaning System

Cleaning of the smog chamber after a photochemical run was accomplished by placing the entire irradiation chamber in a large vacuum chamber and exposing it to a low vacuum of approximately one micron (10^{-3} torr) for a period of approximately 20 hours with the 3" diameter cleanout port and the relief valve port open. In this way, residual products in the chamber are believed to be substantially removed. The vacuum chamber utilized for the cleaning process is located adjacent to the test area. The vacuum chamber consists of an 18 x 18 x 36 ft. main chamber joined to a 10 x 10 x 10 ft air lock chamber. Full access to the 18 x 18 ft opening is obtained by a sliding door. The chamber shell is constructed of 0.5 in. 304 stainless steel and all interior surfaces are polished to a #4 mill finish to facilitate cleaning and avoid impregnation by contaminants. Figure 2-8 shows the smog chamber inside the vacuum chamber.

The chamber pumping system consists of a combination of Roots blowers and Stokes mechanical pumps which allows a high gas load to be easily handled. The Roots blowers are located between the chamber and mechanical pumps which prevents any pump oil from migrating back into the chamber.

Chamber repressurization is controlled manually and is kept to a rate that will prevent the chamber temperature from exceeding approximately 100°F. This repressurization takes approximately 25 minutes. During the repressurization, zero air (hydrocarbons less than 0.1 ppm) is purged through the irradiation chamber. The rate of zero air purge is controlled to ensure that no ambient air enters the irradiation chamber. This is accomplished by monitoring a flow sensor located at the cleanout port of the irradiation chamber. After repressurization, the cleanout port is closed, the relief valve is charged with water, and the irradiation chamber is returned to the thermal enclosure.

2.7 Chemical Analysis Instrumentation

The instrumentation used to determine the reactants and products is described below. A discussion of the actual analytical techniques developed and calibrated for the project is given in Section 3 of this report.

2.7.1 Gas Chromatographs

Beckman GC-4.- The Beckman GC-4 laboratory gas chromatograph is equipped with a helium ionization detector system and a Carle sample valve which allows the sampling of 10-25 cc volume size samples. For the analysis of carbon monoxide, a 20' x 1/8" O.D. molecular sieve 5A (40/60 mesh) stainless steel chromatographic column was installed. The instrument has a low and high temperature linear programmer oven control and a variety of other accessories available for precise applications.

F&M Model 700's.- The F&M 700 series gas chromatographs possess dual columns with flame ionization detector systems, individual temperature controls for the injection ports, column oven, and detector block heat zones. The electrometers on the two units have been replaced with F&M Model 810 electrometers for increased sensitivity. One of the instruments was equipped with

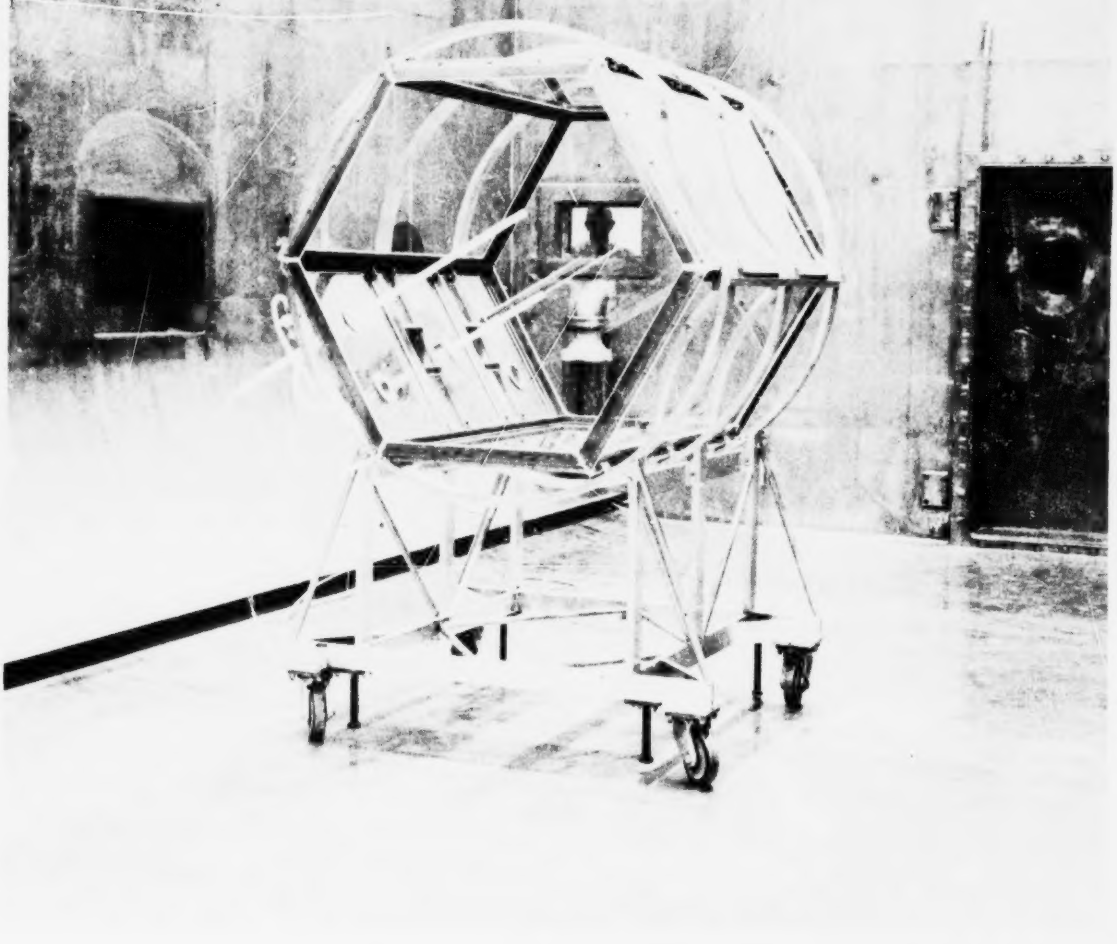

Fig. 2-8 Environmental Chamber Inside Vacuum Chamber

a 2 ft x 1/8" O.D. unpacked stainless steel column and was used for total hydrocarbons analysis. The other unit was used to monitor the propylene and acetaldehyde concentration levels independently with oxygen-hydrogen flame ionization detectors. Propylene was separated on a 20' x 1/8" O.D. stainless steel column packed with 30% equal mixture of di-2-ethyl hexyl sebacate and bis-1 (2-methoxy ethyl) adipate on Chromosorb W while acetaldehyde was separated on a 20' x 1/8" O.D. stainless steel column packed with 10% Ethofat on Chromosorb W.

F&M Model 810.- The F&M Model 810 gas chromatograph is a dual column instrument equipped with dual flame ionization and electron capture detectors. The unit includes an oven temperature programmer ranging from ambient to 450°C and detector blocks and injection port temperature controls. Peroxyacetyl nitrate and ethyl nitrate were analyzed on this instrument by using an electron capture detector and a 27" x 1/8" O.D. Teflon column packed with 5% Carbowax 600 on Chromosorb W (DMSC treated).

This instrument is equipped with two Beckman pneumatically operated gas sampling valves. To prepare concentrated samples for total hydrocarbon constituent analysis, two outlets of a 4-way switching valve were attached to the micro-sample loop connections on one of the Beckman gas sampling valves. A 11" x 1/8" O.D. sorption tube was connected to the other two outlets allowing repeated sample concentration (with liquid nitrogen) and injection into a 12' x 1/8" SS 60-80 mesh Poropak S column. These analyses were performed with the flame ionization detector and were carried out after the test runs.

2.7.2 Continuous Analyzers

Technicon Auto Analyzer.- This unit was modified for continuous analysis of NO_2 by the Saltzmann-Lyshkow wet chemical method. The absorbing columns were two glass coils connected in series (2.4 mm I.D. and 28 turns) and the colorimeter flow cell was 50 mm in path length. The proportioning pump, extended range recorder, liquid/gas separator, and colorimeter were all standard Technicon equipment.

Beckman Model DK-2.- The Beckman Model DK-2 is a double beam system where both sample and reference beams have common detection and amplification components. This unit was used as the colorimeter section for the analysis of NO_x at 550 millimicrons by the Saltzman-Lyshkow method. Two full flow colorimeter cells (15 mm path length) were used, along with a Technicon proportioning pump and liquid-air separator. Similar absorbing columns used in the NO_2

analysis were placed after two oxidizing columns connected in series (6 mm x 19 cm fluted fiberglass paper impregnated with CrO_3-H_2SO_4) used for the oxidation of NO to NO_2.

Mast Oxidant Detector.- The Mast oxidant detector was used to measure total oxidant. It possesses a coulimetric type sensor unit using a 2% KI, 5% KBr phosphate buffered to pH 7.0 solution. Concentration levels were recorded continuously on a Honeywell Electronic 18 variable voltage input recorder, providing attenuations for expanded range readings. Instrument calibration was aided by generating ozone from an Orec ozone generator (Model 03V1).

2.7.3 Other Spectrophotometric Instruments

Perkin-Elmer Model 202 Ultraviolet Visible Spectrophotometer.- The P/E Model 202 ultraviolet-visible spectrophotometer is a double-beam instrument with an automatic gain control and optical-null absorbance coupled system. The two ranges covered are from 190 to 390 millimicrons and 350 to 750 millimocrons. For formaldehyde and total oxidant colorimetric analysis, 8.5-cm path length matched cells were used to obtain the lower limit of detectability requirements.

Perkin-Elmer Model 521 Infrared Spectrophotometer.- The P/E Model 521 is a double-beam grating spectrophotometer possessing a range from 4000 to 250 cm^{-1} (2.5 to 40 microns). The unit is equipped with a high resolution filter grating interchange with automatic gain control, speed suppression, and slit programming. Instrument resolution is 0.3 cm^{-1} at 1000 cm^{-1} and sensitivity varies with compound, sample preparation, and the number of interfering impurities. Accessories include a ten meter, one meter, 7.5 centimeter, 0.75 centimeter (minimum 2.0 cm^3 volume) path length gas cells, ultra-micro 6X beam condenser and direct reflectance and attenuated total reflectance attachment.

2.7.4 Dew Point Indicator

A Cambridge Systems, Inc. Model 992 dewpoint hygrometer can monitor the moisture content from -100°F to +200°F with accuracy of ±1.0°F between -20 and +200°F on a thermistor readout. Above 32°F, the response time is approximately 30F/sec, which is dependent on the cooling/heating rate of the mirror. The sample requirements are from 0.2 - 4.0 SCFH. The instrument is equipped with a two-way inlet valve and a small diaphram pump.

2.7.5 Mass Spectrometer

A Hitachi/Perkin-Elmer model RMU6D possesses a 90° narrow gas magnetic selector (8 in. radius), 7.5 KG field, and 3600 accelerating voltage. Mass range includes 1-1500 with resolution capability M/DM 200-2000 and variable. The unit is equipped with an electron multiplier and Faraday Cup detection system with external precision micrometer type inlet and collector slit controlled from outside the vacuum for resolution control and sensitivity setting. The instrument accessories include a gas chromatograph tandem operation with a Watson-Biemann sample enrichment device, a total ionization monitor, a direct solids introduction system with independent source and sample heat regulation, and a digital data acquisition and computer processing system for identification of compounds.

2.8 Photometric Equipment

For measurement of light intensity and spectral data, a uv monitor and a spectrophotometer were used.

2.8.1 UV Monitor

A commercial uv monitor (Ultra-Violet Products, Inc. J-221) was used. This unit has a peak response at 365 nm, shows a 50% response at 325 and 380 nm, and a 10% response at 305 and 395 nm. It has two scales, 0-12 and 10-50 watt/m^2. It is also equipped with an attenuation screen for use in higher intensity fields. The screen was calibrated using spectrophotometers and found to have an attenuation factor of 4.15.

The commercial meter was calibrated in sunlight against a similar calibrated unit made available by S. L. Kopczynski of the Environmental Protection Agency, and agreed within 7%.

2.8.2 Spectrophotometer

Spectroradiometry was performed using a Beckman DK-2A spectrophotometer. The spectrophotometer was operated in the energy mode, and the light beam reflected into the detectors using a magnesium oxide diffuse reflector. The slit width and gain were adjusted to keep the readings on scale, and provide a comparison to a calibrated quartz-iodide lamp. The quartz-iodide lamp calibration was NBS traceable.

3. ANALYTICAL METHODOLOGY

The analytical methods used for monitoring the various species are presented in Table 3-1. The methods used were, for the most part, those that have been developed previously to perform continuous atmospheric monitoring. Various refinements and adaptations were made to the chamber monitoring requirement of minimizing sample volume consumption.

3.1 Nitrogen Dioxide

Nitrogen dioxide was analyzed by the Lyshkow-modified Saltzman wet colorimetric method using a one-channel Technicon Autoanalyzer unit at concentration levels from 2 to 200 pphm. (Ref. 3-1, 3-2). A schematic of the apparatus is shown in Figure 3-1. The instrument was calibrated statically using $NaNO_2$ solution ranging from 1.5 to 10^{-3} µl NO_2/ml solution to 1.5 x 10^{-1} µl NO_2/ml solution. The NO_2 gas concentration was converted to NO_2 pphm by the following formula:

$$\text{pphm } NO_2 = \frac{(A)(B)}{(C)(D)}\,100$$

where;

A = microliters of NO_2 gas per milliter of liquid standard

$$= \frac{(\text{mg/liter of } NaNO_2)}{(\text{Mol. wt. of } NaNO_2)} \; \frac{(24.5 \text{ liters/mole}}{0.72 \text{ moles } NaNO_2/\text{mole } NO_2)}$$

where 24.5 is the molar volume at 25°C and 760 torr, and 0.72 is the Saltzman factor.

B = flow rate of absorbing reagent (ml/min)

C = air flow rate (liter/min)

D = column efficiency (expressed decimally)

(For static calibration, column efficiency is assumed to be unity.)

In addition, the instrument was dynamically calibrated to determine column absorption efficiency. A NO_2 permeation tube (Metronics Associates, Inc.) was used as the NO_2 gas source (Ref. 3-3). Pre-purified air that had been passed through an activated charcoal bed was flowed over the permeation tube at constant rates. Then the gas mixture was passed through a bottle filled with glass beads, a vented collection bottle and through the absorption columns in the order mentioned. The calculated NO_2 concentration was determined from the following formula:

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TABLE 3-1

ANALYTICAL METHODS

Species	Method	Lower Limit of Detectability (pphm)	Calibration Range (pphm)
NO_2	Lyshkow-Saltzman-Technicon	1	2 - 200
NO	Lyshkow-Saltzman (Chromium Trioxide Paper) Beckman DK-2A	1	2 - 350 Max.
Oxidant	Neutral KI Mast and Colorimetry by Bubbler Sampling	1	10 - 150 (10 and 50 mv range)
Propylene	Gas Chromo. FID	3	5 - 300
Formaldehyde	Chromotropic Acid	3	5 - 240 (Static) 6 liter volume sample size
Acetaldehyde	Gas Chromo.-FID	2	8 - 170
PAN	Gas Chromo.-ECD	2	5 - 100
Carbon Monoxide	Gas Chromo.-HID	5	10 - 300
Ethyl Nitrate	Gas Chromo.-ECD	2	---
Water	Dew Point	-80°F	-80°F to 120°F

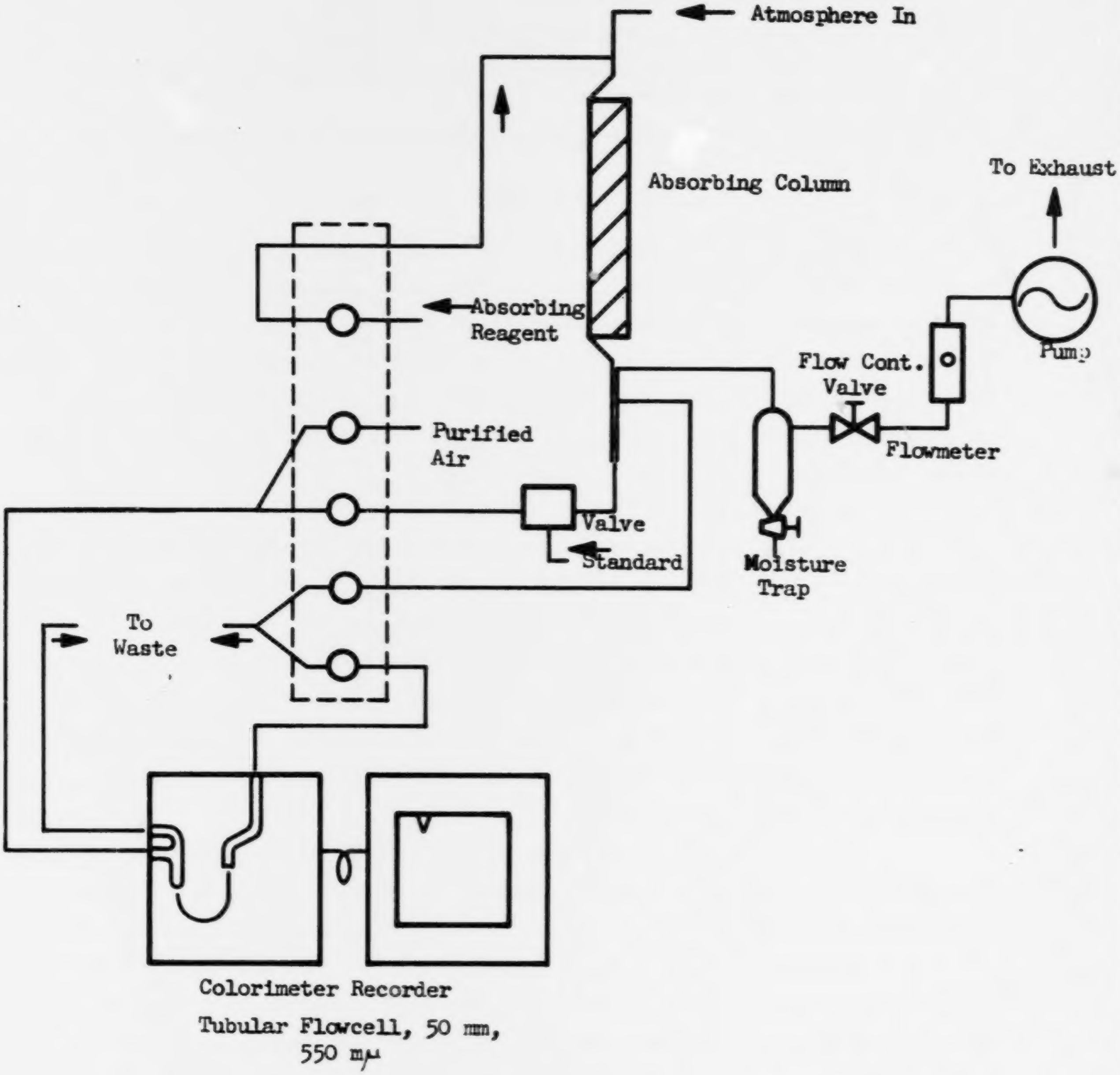
Atmosphere In
Absorbing Column
To Exhaust
Absorbing Reagent
Pump
Flow Cont. Valve
Purified Air
Flowmeter
Valve
Standard
Moisture Trap
To Waste
Colorimeter Recorder
Tubular Flowcell, 50 mm, 550 mμ

Fig. 3-1 NO_2 Analysis Schematic

$$C = \frac{(L)(K)(Pt)}{F} 100$$

where:

C = gas concentration (pphm)

L = length of permeation tube (cm)

K = molar volume/molecular weight = 0.532 for NO_2 at 25°C and 760 torr (liter/gm)

Pt= permeation rate of NO_2 at temperature t (ng/min per cm of tube length)

F = carrier gas flow past tube (cm^3/min)

For two 15 cm x 0.2 cm I.D. (28 coil turns) glass columns connected in series, a 96% column absorption efficiency was obtained. This value was constant at concentration levels from 7 to 150 pphm NO_2. Precision evaluated under static conditions ranged from 5% at 2 pphm to 1% at 100 pphm NO_2. Precision is defined throughout this report as percent relative standard deviation, obtained as a percentage equal to 100 times the standard deviation of a series of replicates, divided by the mean of the replicates.

3.2 Nitric Oxide

The analytical methodology used for nitric oxide (NO) analysis was the same as used for determining the NO_2 levels except that the sample was passed through an oxidizer column prior to passing through the absorption column.

The apparatus used for NO analysis is shown in Figure 3-2.

The nitric oxide was oxidized to NO_2 and the total value was reported as NO_x. NO was reported by difference between the total NO_x measured and the NO_2 measured simultaneously by the Technicon Auto Analyzer, from continuous samples obtained in the same sampling location.

The colorimeter used for NO was a Beckman DK 2A spectrophotometer with a double-flow cell sampling set up whereby the absorbing solution was passed through the reference cell prior to entering the absorbing column.

Both static and dynamic calibration runs were made on the system. Static calibrations were followed using the same techniques for NO_2, while dynamic calibrations were made from diluting known NO levels in pressurized nitrogen bottles. Precision on static calibration runs ranged from 8% at 2 pphm to 2% at 100 pphm.

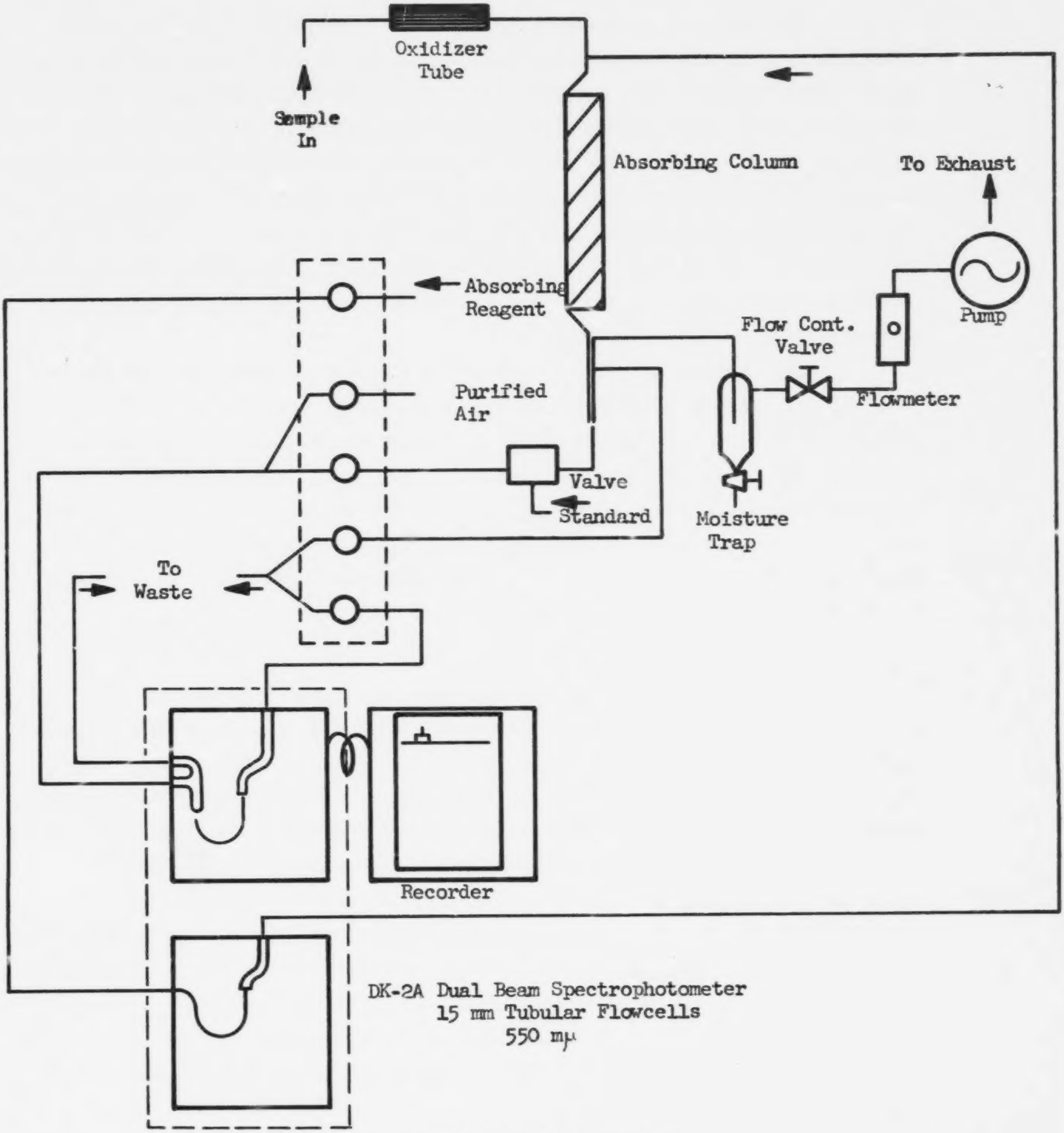
Oxidizer Tube
Sample In
Absorbing Column
To Exhaust
Absorbing Reagent
Pump
Flow Cont. Valve
Purified Air
Flowmeter
Valve
Standard
Moisture Trap
To Waste
Recorder
DK-2A Dual Beam Spectrophotometer
15 mm Tubular Flowcells
550 mμ

Fig. 3-2 NO Analysis Schematic

The various oxidizing techniques tried were $KMnO_4$-H_2SO_4 bubbler solution, CrO_3 on alundum spheres, rolled CrO_3 on tightly packed fiberglass paper (Scott Research Co.) and CrO_3-H_2SO_4 on fluted fiberglass paper (Mast Development Co.). The method that was the most effective was two fluted CrO_3-H_2SO_4 on fiberglass paper tubes connected together after pre-conditioned in humidified air until the tubes had turned color from pink to yellow. Oxidation efficiency was established at 100% for NO alone and in the presence of NO_2. Dynamic calibrations were run using both NO in nitrogen and the NO_2 permeation tube source diluted with air to verify this value. Table 3-2 summarizes the results obtained.

The accuracy of this method was determined by assuming that the dilution formulasfor NO and NO_2 concentrations were correct, and that the permeation tube NO_2 yields were correctly given by the calibration formula supplied. (NO_2 was cross-checked by a stock NO_2-in-nitrogen cylinder). Instrument parameters for accuracy evaluation were measured by a precision wet test meter for air flows to the instrument, class A volumetric flasks for liquid flow measurements, a stopwatch and calibrated rotameters in the range 70-18,400 cc/min nominal air flow rate for NO and NO_2 dilution.

3.3 Oxidant (Ozone)

The oxidant level was monitored by two techniques; (a) the Mast Model 724-2 ozone meter and (b) colorimetric analysis on batch samples. Both techniques used a buffered 2% KI solution; for the Mast, this solution flows through a microcoulimetric cell, while for the batch analysis, the gas being analyzed is bubbled through the solution, and colorimetric analysis performed.

Colorimetric procedures followed those of Ref. 3-4. Samples for colorimetric analysis were drawn into midget impingers containing the KI solution. Quantification was carried out on the Perkin—Elmer 202 spectrophotometer at 350 $m\mu$, using 1-cm path length silica glass cells. The KI solution was calibrated with a stock I_2 solution, using titration against $Na_2S_2O_3$ solution. The equivalence factor used was 12.25 ml ozone per milliequivalent of I_2. The I_2 solutions were added to the KI solution and run on the spectrophotometer. A Beer's law plot was developed.

TABLE 3-2
OXIDATION EFFICIENCY DATA FOR NITRIC OXIDE
CrO_3-H_2SO_4 FIBERGLASS TUBES

NO_2			NO			NO_x		
Measured*	Calculated	% Measured/Calculated	Measured*	Calculated	% Measured/Calculated	Measured*	Calculated	% Measured/Calculated
--	--	--	231 pphm	235 pphm	98	231 pphm	235 pphm	98
--	--	--	138	135	102	138	135	102
82 pphm	83 pphm	99	70	70	100	152	153	99
100	97	103	69	70	99	169	167	101
22	22	100	17	18	95	39	40	98
16	17	95	13	13	100	29	30	98
16	17	95	14	13	108	30	30	100
25	25	100	17	18	95	42	43	98
25	25	100	24	24	100	50	49	102
	Mean	98.8			99.7			99.5
	Std. Deviation	3.0			4.4			1.5

*Measured as referred to static calibration.

The Mast was calibrated against the colorimetric method in a range of 10 to 200 pphm. To obtain readout over 100 pphm, a multi-range recorder was used. In the absence of other oxidants, instrument lower limit of detectability was 2 pphm. Precision was less than 3%. For the calibration, an OREC ozone generator was used to produce O_3 in air, which was fed to a sampling bottle where it was diluted with air to the desired concentration. Simultaneous sampling was used for the Mast and the colorimetric bubbler to give a direct correlation. Chamber samples were drawn from the manifold through Teflon tubing by the instrument's sample pump at a nominal 140 cc/min rate, previously verified using a wet test meter. It was observed that the Mast output was sensitive to chamber pressure variations to the extent of about 2%, presumably because of variations in sampling rate as chamber pressure changed.

Response of the Mast instrument to NO_2 was determined by flowing known NO_2 concentrations (prepared using the permeation tube). Data are shown below:

NO_2 Concentration pphm	Mast Reading pphm	NO_2 Response Factor
21	2	10.5
29	2	14.5
49	3	16.4
75	5.5	13.6
91	7.5	12.3
208	10	20.8
	Mean	14.7
	Standard Deviation	4.1

This response factor is reasonable. The literature reports values of 20 (Ref. 3-4), 10 (Ref. 3-5) and 8.8 (Ref. 3-6) for this factor.

3.4 Propylene

Propylene was analyzed by gas chromatographic techniques on the F&M Model 700 instrument (Model 810 electrometer) equipped with a 20' x 1/8" O.D. stainless steel column packed with 30% equal mixture of di-2-ethyl hexyl sebacate and bis-2 (2-methoxy ethyl) adipate on 60/80 mesh Chromosorb W at a

60°C oven temperature. The detector temperature was set at 125°C while the injection port was set at 105°C. An O_2-H_2 flame was used for increased sensitivity. Ten cc volume size samples were injected into the chromatograph with Hamilton gas-tight syringes. These samples were obtained from 500 cc volume glass bottles which were filled with chamber gas by attaching evacuated bottles to the chamber sampling manifold and by opening the stopcock to the chamber atmosphere. Linear calibration curves were developed from 5 to 300 pphm. Precision at 300 pphm was less than 5%.

3.5 Carbon Monoxide

Carbon monoxide analysis techniques were developed for measuring in the 5-300 pphm range by gas chromatography using a Beckman model GC-4 equipped with a helium ionization detector unit. For this chromatograph ultra-pure grade helium (Linde Air Products) was used as the carrier gas. This particular method was selected due to the high sensitivity at minimum volume sample consumed. Carbon monoxide was separated from the other gaseous constituents on a 20' x 1/8" O.D. stainless steel column packed with 40/60 mesh molecular sieve 5A. The oven was operated at 75°C while the detector temperature was maintained at 115°C. The carbon monoxide absolute retention time was ten minutes. Samples were introduced via a Carle gas sampling valve which was continuously purged with helium to prevent backflow air leakage. A 20 cc volume sample size was required to detect 5 pphm.

Precision was less than 5% at 300 pphm.

3.6 Formaldehyde

Formaldehyde was analyzed by the modified chromotropic acid method using the Perkin Elmer Model 202 spectrophotometer (Ref. 3-7, 3-8). Six liter volume samples were bubbled through chromotropic acid solution. The bubblers containing the samples were sealed with polyethylene film and placed in a refrigerator overnight. The samples were run the following day. Calibration curves were obtained by using sodium formaldehyde bisulfite solutions following the procedures outlined by the Bay Area Pollution Control District (Ref. 3-9), On a six liter volume sample, the lower limit of detectability was 3 pphm.

3.7 Acetaldehyde

Acetaldehyde was analyzed on the same F&M Model 700 (equipped with Model 810 electrometer) dual flame O_2-H_2 ionization detector gas chromatograph used for propylene analysis, Propylene was analyzed on the B or lower detector unit while acetaldehyde was analyzed on the A or upper detector with a separate F&M Model 810 electrometer and recorder readout unit. Acetaldehyde was separated from the other constituents by a 20' x 1/8" O.D. stainless steel column packed with 10% Ethofat substrate on Chromosorb W (Varian-Aerograph). Oven, detector, and injection port temperatures were the same settings that were used for the propylene analysis. Samples (10 cc) were drawn from 500 cc volume bottles obtained from the chamber manifold. The lower limit of detectability was 2 pphm. Calibration curves were established from 8-170 pphm. Precision at 150 pphm was less than 10%.

3.8 Peroxyacetyl Nitrate/Ethyl Nitrate

Peroxyacetyl nitrate (PAN) analysis and ethyl nitrate estimation levels were measured by gas chromatographic analysis techniques on an F&M Model 810 instrument equipped with an electron capture detector and a 27" x 1/8" O.D. Teflon column packed with 5% Carbowax 600 on 80/100 mesh Chromosorb W (LMSC treated). Helium was used as a carrier gas and oven, detector, and injection port temperature were maintained at ambient conditions. Instrument calibration for concentration levels were established by the production of PAN from ethyl nitrite ultraviolet irradiation in a 10 cm path length infrared gas cell (Ref. 3-10).

Varying volume sample sizes up to one cc were used for analysis in the range from 2-200 pphm. Samples were drawn directly from the chamber manifold with 1 cc gas tight volume syringes and indirectly from samples drawn from the chamber manifold via 500 cc volume evacuated Pyrex bottles.

3.9 Moisture (Water)

Moisture content was monitored with a Cambridge Industrial Hygrometer Model 992. Samples were drawn periodically from the chamber manifold through a two-way sampling valve. Otherwise, room air was purged through the instrument allowing continuous instrument readout. Stable instrument response at 250 cc/min sample flow was less than 3 minutes for dew point ranging from 48°F to 56°F. Precision was less than 0.1% based on saturation pressure.

3.10 Total Hydrocarbons

Chamber background hydrocarbon levels were monitored with an F&M Model 700 gas chromatograph equipped with a flame ionization detector unit and an unpacked 1/8" O.D. stainless steel column. Samples were drawn from the chamber with evacuated 500 cc volume sampling flasks. Gas tight syringes were used to transfer and introduce samples from the sampling flasks into the gas chromatograph.

Calibrations were made with methane mixed in zero air on the assumption that each hydrocarbon present gives a response proportional to its number of carbon atoms. The same zero air was used for purging the chamber and for starting the chamber runs. Background response contributed by zero air was deducted from the calibrated methane response and chamber samples analyzed.

3.11 Detailed Hydrocarbons

The composition of the hydrocarbons in the chamber prior to and after the test was analyzed by programmed gas chromatography using a flame ionization detector and a 12' x 1/8" O.D. stainless steel column packed with Poropak S (Waters Associates). Freeze-trap concentration of 500 cc volume samples was used prior to introducing the samples into the column. A diaphragm pump pulled the sample through an absorbing column (11" x 1/8" O.D. stainless steel column packed with 60/80 mesh Chromosorb W) that was cooled at liquid nitrogen temperatures. The absorbing column was allowed to warm up to room temperature before transferring the flow from the absorbing column into the gas chromatograph column. The analysis column is temperature programmed for room temperature to 225°C at 2°C/min.

This technique detects essentially all common hydrocarbons with boiling points below about 140°C. Unsaturated aliphatics below hexene are detectable at less than 1 pphm lower limit of detectability. Alcohols, aldehyde, ketones, and organic acids are also detectable at about 5 pphm lower limit of detectability. The technique is demonstrated by the listing in Table 3-3 of retention time data.

Table 3-3

ABSOLUTE AND RELATIVE RETENTION TIME DATA* (Ref. 3-11)

Compounds	Boiling Point °C	Oven Temperature °C	Absolute Retention Time (Min.)	Relative Retention** (Freon 12)	Relative Retention*** (Benzene)
Methane	-161.5	28	2.0	0.054	
Ethylene	-103.9	28	9.4	0.258	
Genetron 23	- 82.0	28	9.6	0.261	
Acetylene	- 83.6	28	11.5	0.313	
Ethane	- 88.3	40	13.2	0.354	
Propylene	- 47.0	73	31.0	0.840	
Propane	- 42.2	77	32.8	0.885	
Freon 22	- 40.8	79	32.9	0.887	
Allene	- 32.0	80	33.9	0.922	
Methyl Chloride	- 24.2	80	34.4	0.930	
Cyclopropane	- 34.4	81	34.8	0.940	
Propyne	- 23.3	82	35.4	0.957	
Freon 12	- 29.8	86	37.0	1.000	0.427
Vinyl Chloride	- 13.9	101	44.0	1.190	
1, 3-Butadiene	- 3.0	101	44.0	1.190	
Methyl Alcohol	64.7	104	45.0	1.240	0.519
Isobutane	- 10.2	110	48.4	1.320	
Isobutylene	- 6.9	111	49.8	1.352	
1-Butene	- 5.0	112	50.0	1.373	
Acetaldehyde	21.0	113	51.1	1.380	0.587
Freon 114	3.8	116	51.2	1.410	
n-Butane	- 0.6	116	51.2	1.410	
t-Butene-2	2.5	116	52.3	1.415	
Genetron 21	8.9	124	56.6	1.554	
Ethyl Alcohol	78.5	129	58.9	1.600	0.684
Freon 11	23.8	134	61.8	1.680	0.717
Propionaldehyde	48.8	134	61.9		0.718
Acetone	56.5	135	62.6	1.710	0.721
Chloroacetone	119.0	136	63.2	1.720	0.727
Methylene Chloride	40.1	138	64.7		0.740
Isoprene	34.0	145	67.8		0.786
Isopropyl Alcohol	82.3	145	67.8		0.786
n-Pentane	36.2	146	68.8		0.791
Chloropropane	47.2	149	70.4		0.810
Cyclopentane	49.5	151	71.4		0.821
cis-Dichloroethylene	60.1	158	75.1		0.862
n-Propyl Alcohol	97.2	160	75.6		0.870
Butyraldehyde	75.7	163	77.6		0.900
Methyl Ethyl Ketone	79.6	165	79.6		0.916

Table 3-3

ABSOLUTE AND RELATIVE RETENTION DATA (Ref. 3-11)

(Continued)

Compounds	Boiling Point °C	Oven Temperature °C	Absolute Retention Time (Min.)	Relative Retention (Freon 12)	Relative Retention (Benzene)
Ethyl Acetate	77.2	167	81.2		0.935
Dimethyl Butane	49.7	170	81.8		0.942
3-methyl Pentane	64.0	170	81.8		0.942
n-Hexane	69.0	172	83.2		0.957
1,1,1 Trichloroethane	74.1	177	85.0		0.977
Methyl Cyclopentane	71.8	177	85.0		0.977
1-Hexene	63.5	178	85.2		0.982
Benzene	80.1	181	87.0	2.35	1.000
Cyclohexane	81.4	183	88.4		1.016
Trichloroethylene	87.0	184	89.1		1.020
Cyclohexene	83.0	184	89.1		1.020
n-Butyl Alcohol	117.7	186	89.4		1.040
1,4 Dioxane	101.5	186	89.4		1.040
2-Pentanone	101.7	189	91.0		1.046
3-Pentanone	102.7	189	91.0		1.046
Ethyl Sulfide	92.0	191	92.6		1.070
n-Heptane	98.4	199	95.0		1.100
Methyl Cyclohexane	100.3	201	97.0		1.115
Propyl Acetate	101.6	203	98.3		1.130
Tetrachloroethylene	121.0	203	98.6		1.135
Methyl Isobutyl Ketone	119.0	206	99.7		1.147
Toluene	110.6	208	100.4		1.160
Ethyl Benzene	136.2	214	106.0		1.240
Chlorobenzene	132.0	222	110.3		1.260
m-Xylene	139.1	224	111.5		1.270

** Retention relative to Freon 12 = 1.000

*** Retention relative to benzene = 1.000

*Conditions:
1/8" x 12' SS column packed with 50-80 mesh Porapak S. 12 minutes ambient at 28°C, 2°C per minute temperature programmed to 225°C, then isothermal. Detector temperature, 200°C; injection port temperature, 210°C. Helium carrier gas (14.5 cc/min); 57 psig inlet pressure. F&M Model 810 equipped with linear temperature programmer and flame ionization detectors (Ref. 3-11).

4. CHAMBER CHARACTERISTICS

Experimental checkout of the chamber before the actual photochemical runs was extensive. Direct determinations were made of: nitrogen dioxide (NO_2) photolysis rate (duplicate determinations); NO_2 absorption by the chamber; concentration gradients and dynamic leak rate; ozone halflife in the dark (duplicate); and ozone halflife in the light (duplicate). A dummy run, in which the chamber was brought to temperature, charged with reactants, and monitored for reaction products and reactant decay, was performed. In addition, the illumination intensity and spectral distribution was studied for several locations, including one at the front face of the chamber and one at the rear of the chamber. These chamber characteristics investigations are discussed below.

4.1 Chamber Leakage

Chamber leakage characteristics were established by several techniques which include pressure decay measurements, determination of steady-state inflow at a fixed chamber pressure, and measurement of the dilution rate of an inert constituent. The results of these various measurements are summarized in Table 4-1 and are discussed below. As can be seen from the table, good agreement was obtained from the various techniques. The pressure decay tests were performed by pressurizing the irradiation chamber to 0.5 inches of water, shutting off all inflow and observing the rate of pressure decay. The pressure decay rate of an average chamber pressure of 0.20 inches of water was 0.023 inches of water per minute, which results in a leak rate of 0.75 percent/hour. The decay rate at an average pressure of 0.10 inches of water was 0.050 inches of water per minute which results in a leak rate of 0.34 percent/hour. These data are presented in Figure 4-1.

TABLE 4-1
ENVIRONMENTAL CHAMBER LEAKAGE CHARACTERISTICS

Technique	Average Chamber Pressure in H_2O	Observed Leak Rate Percent per Hour*
Pressure decay	0.10	0.34
Pressure decay	0.20	0.74
Steady-state makeup	0.10	0.39
Steady-state makeup	0.22	0.83
Methane dilution	0.22	0.82

*Percent of the chamber volume of 1864 liters.

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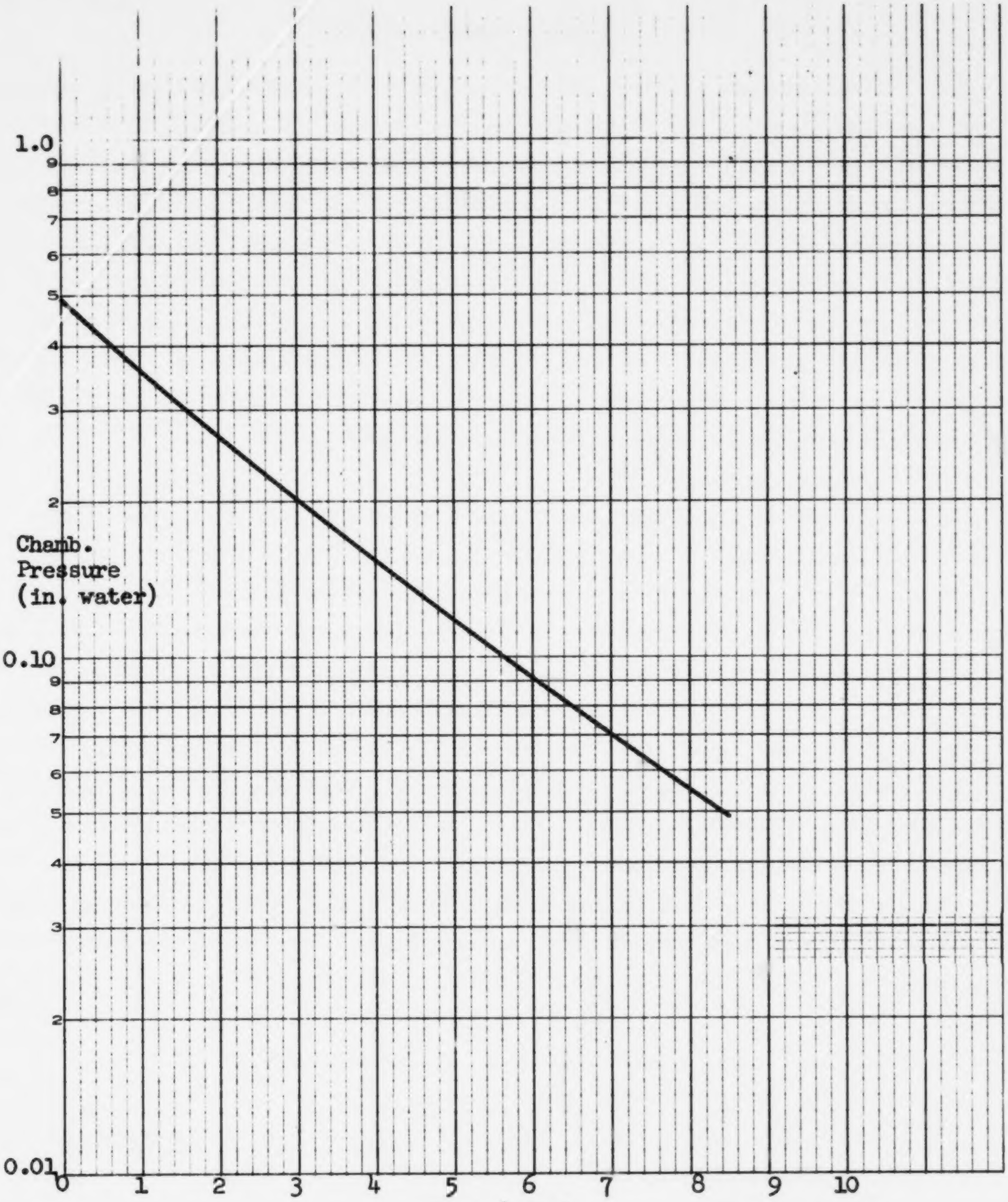


Fig. 4-1 Chamber Pressure Decay

Leakage tests were also conducted on the basis of monitoring the makeup gas required to maintain the chamber at a fixed average pressure. During the first test (NO_2 absorption), the chamber makeup gas flow was monitored for 300 minutes. The average chamber pressure was 0.1 inches of water. Using a wet test meter, makeup flow was measured as 156 liters. The sampling rate for gas analysis during this test was 400 ml/min which results in 120 liters for sampling. Chamber leakage was then 36 liters, giving an 0.39% per hour leak rate.

In a second test, also conducted for 300 minutes (methane dilution), the makeup gas addition was 265 liters with 187.5 liters withdrawn for gas sampling resulting in a total leakage of 77.5 liters. This test was conducted at an average chamber pressure of 0.22 inches of water and the resultant leak rate was 0.83 percent per hour.

The final technique utilized for establishing chamber leakage was to monitor directly the decay rate of methane, an inert constituent, while maintaining chamber pressure with a methane-free makeup gas. The results of this test are presented in Figure 4-2, which presents the methane decay for 300 minutes at a chamber average pressure of 0.22 inches of water. A fairly smooth downward trend in concentration is shown by the data. The precision of the data is estimated at ±5%. To obtain the initial methane concentration, the readings at 10, 15, 20, and 30 minutes for both sample locations were averaged. This yielded 1336 ppm. The final methane concentration was obtained by averaging the duplicate determinations for both sample locations, yielding 1158 ppm. This gives an observed dilution factor of 0.867. Scaling this against the dilution factor observed from the wet test meter produces a leakage rate of 0.82% per hour.

4.2 NO_2 Photolysis Actinometry

The photolysis of NO_2 in nitrogen has been used extensively as a measure of the intensity of light in the wave length interval of interest for smog chambers, since its popularization by Tuesday (Ref. 4-1). As pointed out by Altshuller and Bufalini (Ref. 4-2), the method is rapid and convenient; however, it weights the longer wave length region of the 300 to 400 nm sensitive interval more highly than the shorter region. Thus, it should be used in conjunction with energy distribution data. It is interesting to note

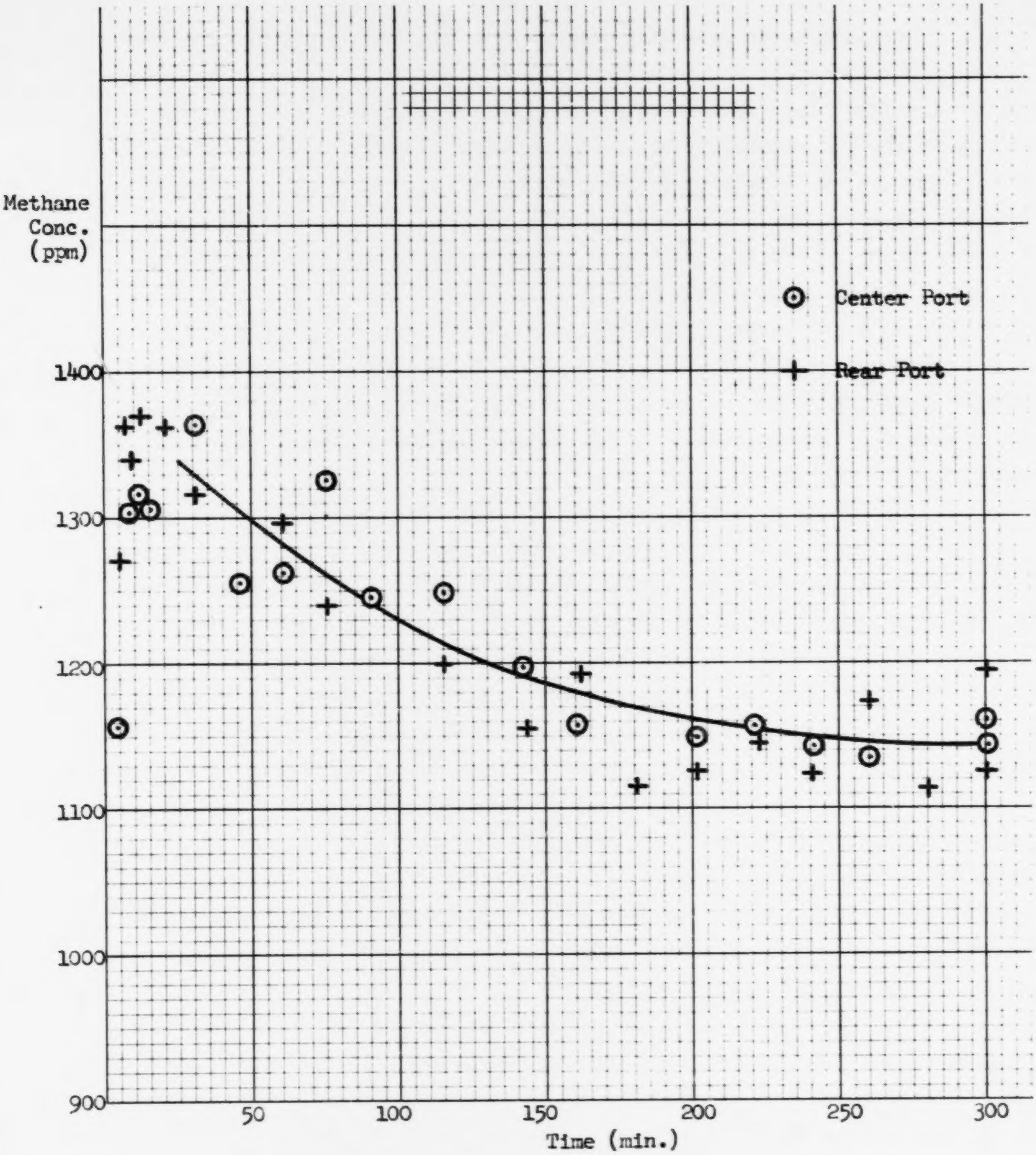


Fig. 4-2 Methane Dilution

that an alternate convenient actinometry method, photoisomerization of o-nitrobenzaldehyde (ONBA) weights the shorter wavelengths more strongly (Ref. 4-3). Although both NO_2 and ONBA actinometry were used in exploratory studies, chamber actinometry was accomplished by NO_2 photodissociation, as this technique automatically gives a true volumetric average for the smog chamber, and furthermore, appears to be more directly related to the photochemical reactions of interest.

Method - The chamber is purged with nitrogen to remove residual NO_2 and reaction products, and to bring the oxygen level to less than 100 ppm and total hydrocarbons to less than 2 ppm. Thermal enclosure heaters and fan are energized to bring the chamber to 95°F, as measured by the chamber thermocouple. The chamber mixer is turned on and NO_2 in nitrogen is charged to bring the chamber to about 2 ppm NO_2. After stable NO_2 content is indicated by the instruments (20 to 35 minutes after charging), the chamber mixer is turned off. The illuminator is shuttered off from the chamber, turned on, and allowed to stabilize as during the first 5 minutes of lamp operation, it is coming up to temperature, and the output varies by perhaps 5% during this time. When illuminator stability is reached, the chamber is illuminated for two minutes. The new stable NO_2 concentration is recorded after a minimum waiting time of 20 minutes. A second and third illumination is then performed in a similar manner.

Sampling of oxygen content is by means of flowing a sample stream through 3/8 inch Polyflow tubing from the chamber to the gas sampling loop of a gas chromatograph equipped with an electron-capture detector.

Results - Two separate tests were conducted. Data were analyzed in the conventional manner, by a plot of the logarithm of NO_2 concentration vs illumination time. Figs. 4-3 and 4-4 show the results. The apparent first order reaction rate constant K_d is calculated from:

$$K_d = \frac{1}{t} \ln \frac{(NO_2)_i}{(NO_2)_f}$$

where t = illumination time

$(NO_2)_i$ = initial NO_2 concentration

$(NO_2)_f$ = final NO_2 concentration.

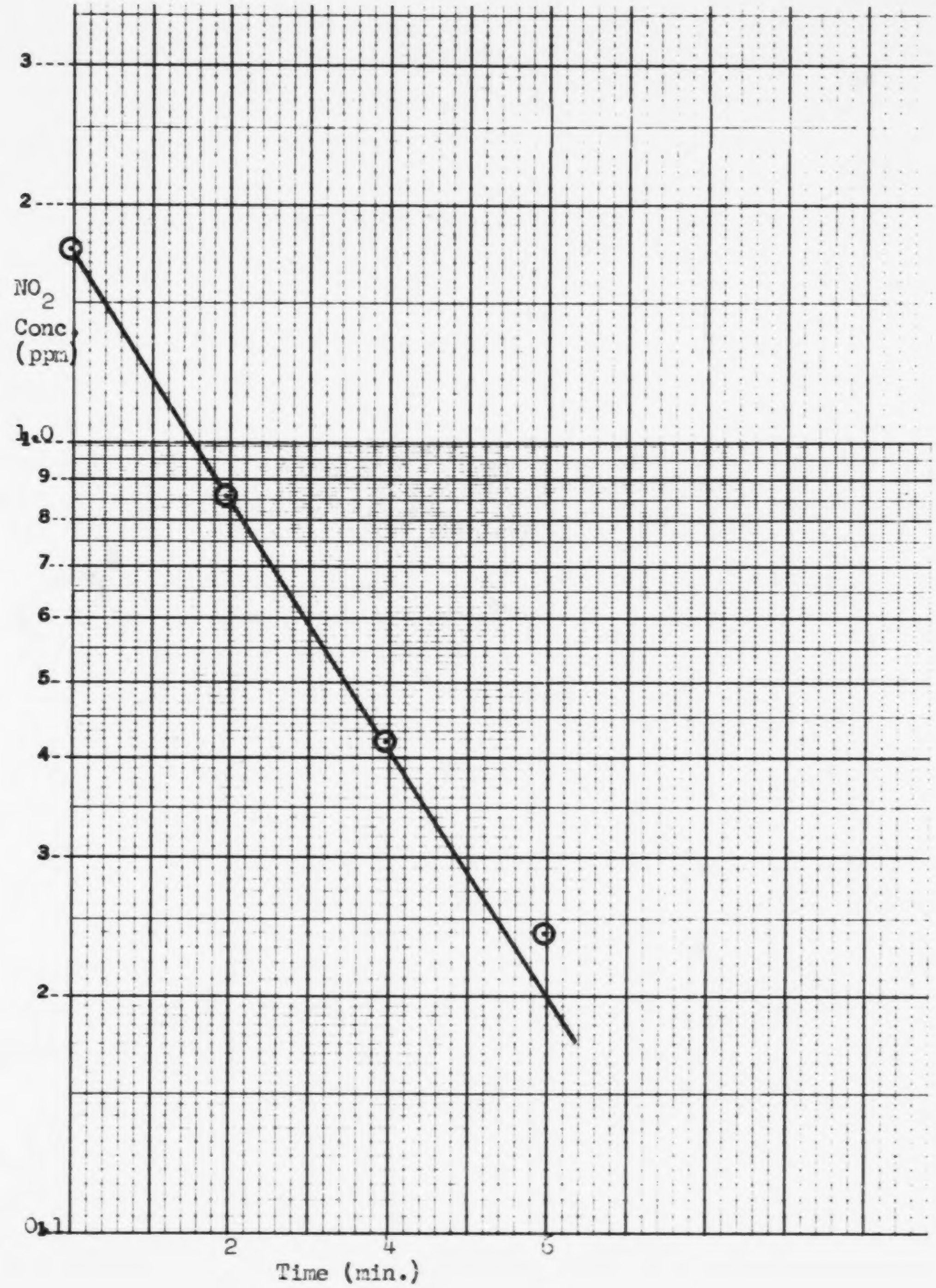


Fig. 4-3 NO_2 Photolysis

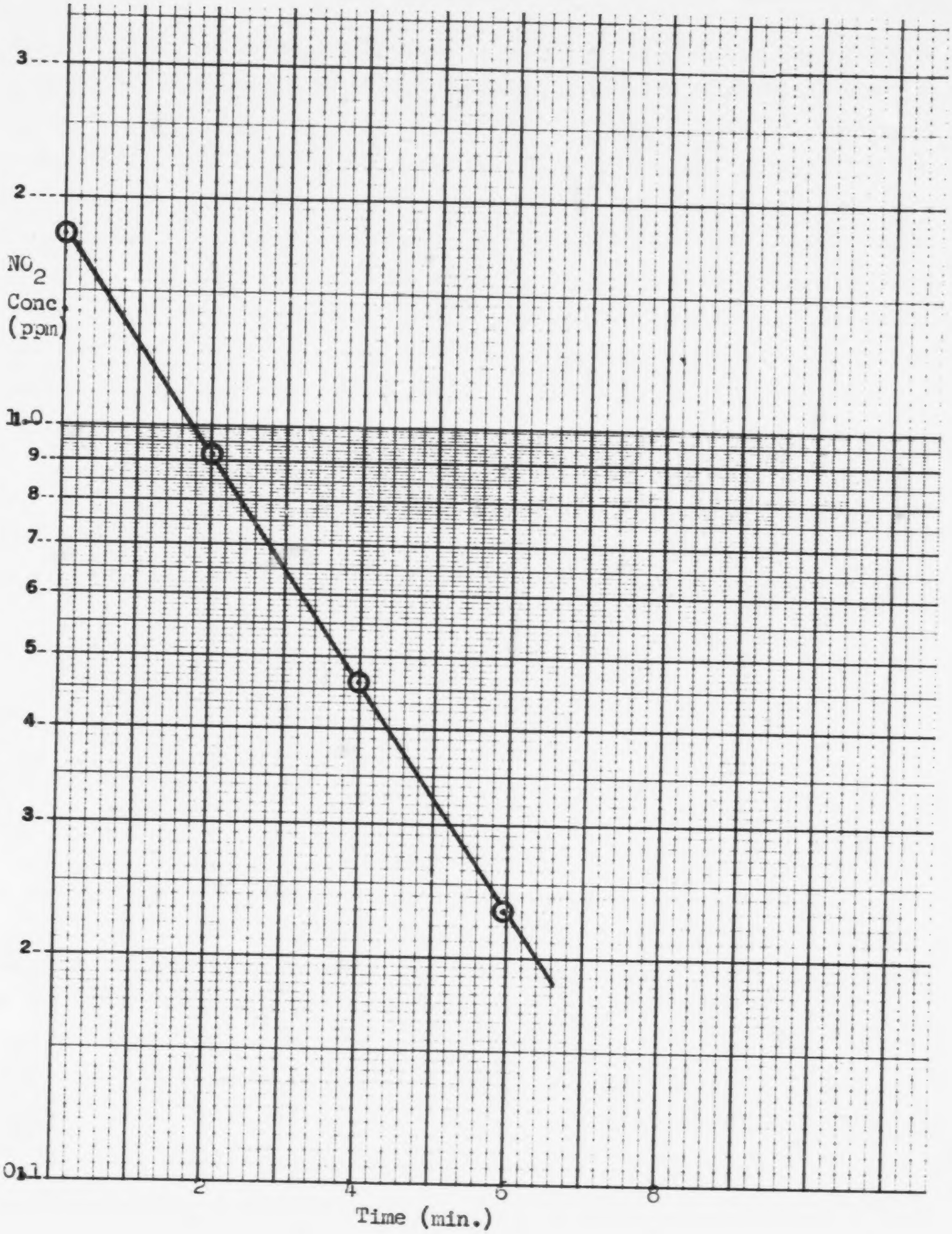


Fig. 4-4 NO$_2$ Photolysis

A convenient calculation procedure is to find $t_{\frac{1}{2}}$, which is the time for NO_2 concentration to be reduced to one-half of the initial concentration, which gives $K_d = 0.693/t_{\frac{1}{2}}$ directly. The semilog plots gave a good straight line for illumination periods of 4 or 6 minutes, compared to the halflife of about 2 minutes, indicating that back-reactions did not affect the K_d value. Some smog chamber operators (Ref. 3-6) photolyze for a series of shorter periods, such as one minute, and obtain a curved semilog plot of NO_2 concentration vs time, which is then extrapolated to obtain the initial photolysis rate. The two minute interval procedure would give a lower K_d (if it gives any different results) and is consistent with that used by the CRC-CAPI-6-69 project group. Table 4-2 gives the results.

TABLE 4-2
NO_2 PHOTOLYSIS

Date	Lamp Power (Watts)	Initial O_2 (ppm)	Hydrocarbons (ppm as methane)	K_d (per minute)
12/21/71	6700	100 ± 15	0.1	0.34_5
12/22/71	6700	100 ± 15	0.1	0.35_6

Discussion - The K_d values obtained showed good experimental agreement, and a value of 0.35 per minute is reported for the smog chamber. Previous work with a different reflector had shown good experimental agreement for a set of three replicates, so it was not considered necessary to do more than two replicates with the present reflector.

The feasibility of obtaining a higher photolysis rate was also investigated. An existing front surfaced plane mirror was mounted behind the smog chamber, to obtain a second pass of light through the chamber. The value of K_d was increased about 40% by the use of this back mirror. It was decided not to use the back reflector mirror, as its effect on spectral distribution was not known, and it would complicate the spectroradiometric measurements. However, another K_d run at reduced illumination power level made in investigating the back mirror did show that K_d was linear with power to within a few percent with about a 20% reduction in power.

4.3 NO_2 Absorption

Method - Laboratory air is passed through a charcoal sorption bed, through a humidifying column and into the smog chamber. Chamber air criteria are: less than 2 ppm hydrocarbons, 95 ± 3°F air temperature and 25 ± 5% relative humidity (54 ± 6°F dew point). When these conditions are obtained, the chamber mixer is turned on, and NO_2 in nitrogen charged to bring the chamber to about 2 ppm NO_2. The chamber is darkened. A wet test meter is put in line to record makeup zero air flow. Chamber contents are sampled by the NO_2 monitor and the dew point monitor. The mixer is turned off 1/2 hour after charging.

Results - The test was conducted as described above. The initial total hydrocarbons were 0.2 to 0.3 ppm as methane. Half-way through the test and at the conclusion of the test, the analysis was 0.2 ppm total hydrocarbons as methane, of which 0.1 ppm is methane.

Chamber temperature was 95 to 98°F, dew point increased from 54 to 56.5°F, chamber pressure varied from 0.25 to 0.02 inch water, with an average pressure of about 0.1 inch. The initial NO_2 was 1.90 ppm, which decreased smoothly to 1.71 ppm over the 5-hour run, (Figure 4-5) for an observed concentration decay of 10%. A wet test meter was used to determine makeup gas flow, and the total gas added to the chamber determined to be 156 liters (uncorrected for the minor temperature and pressure variation from STP). Approximating the smog chamber as a well-stirred flow reactor, the concentration decay is given by $C = C_o \exp(-Ft/V)$ where F = flow rate, t = time, V = volume. For Ft = 156 liters, V = 1864 liters, final concentration would be 0.920 of the initial concentration. The observed difference in concentration decay of 2.0% is reported as the NO_2 absorption over the 5 hour run.

4.4 Concentration Gradient and Dynamic Leak Rate

Method - The chamber is purged with laboratory air, and a background methane concentration obtained. The chamber is brought to 95°F and the mixer turned on. A sample outflow rate of about 500 ml/min is set through the manifold. Methane is added, using the same pressurized sampling cylinder technique used to charge the other reactants. Samples are taken from the manifold and from an end sample tube simultaneously on the following schedule: 2, 4, 6, 8, 10, 15, 20, 30, 45, 60, ... minutes after charge.

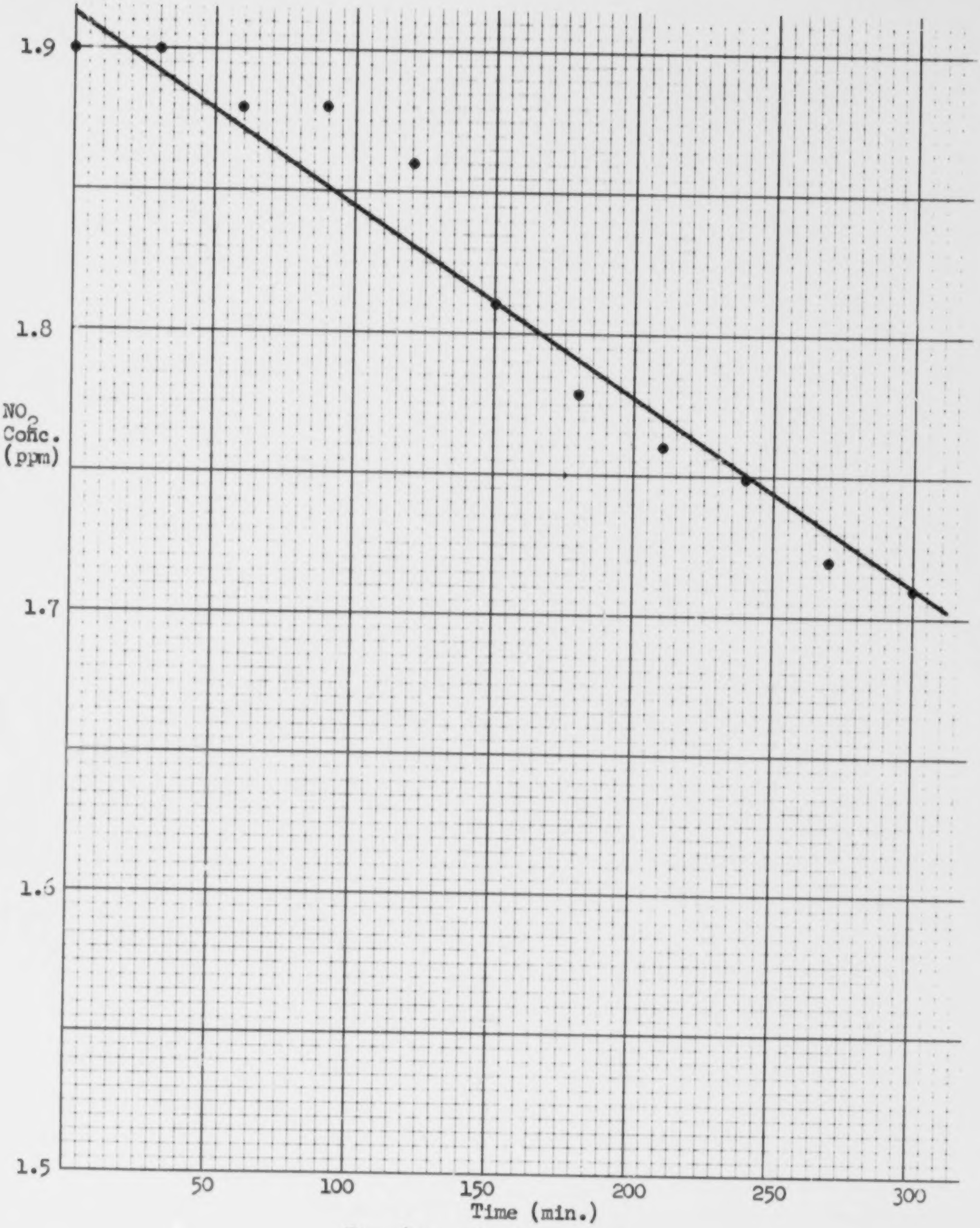


Fig. 4-5 NO_2 Absorption

The end sample tube is installed in the chamber port normally used for the thermocouple probe and consists of a 1/4-inch Polyflow tube brought through the chamber port and outside the thermal enclosure. Sampling from the manifold is by a pre-evacuated 500 ml gas sample bottle. The volume of the manifold sample system is about 740 ml, so the outflow rate of 500 ml/min maintains representative contents in the manifold. Volume of the end sample tube system is about 130 ml; a 500 ml gas sample is drawn and discarded immediately before the actual sample is taken.

Results - Figure 4-6 shows the methane concentration transient upon charging. Mixing appears to be complete 6-8 minutes after charging. Dynamic leak rate results have already been discussed in Section 4.1 and were shown in Figure 4-2.

4.5 Ozone Halflife in the Dark

Method - The chamber is purged with purified bottled air (air flow through a charcoal sorbent bed) and with ultra zero grade air until the specified maximum hydrocarbon content of 0.1 ppm unsaturated hydrocarbons is attained. Ozone is generated using an OREC ultraviolet generator being fed oxygen, and the ozone-oxygen mixture placed in a Tedlar transfer bag. The smog chamber mixer is turned on, and the ozone introduced into the chamber to attain about 1 ppm ozone. The chamber is darkened. The chamber mixer is shut off about 30 minutes after ozone introduction. Chamber leakage and sample withdrawal is compensated for by zero air makeup through a wet test meter. Chamber temperature is maintained at 75°F ± 3°F and pressure is kept at 0.1 ± 0.05 inch water.

Ozone is monitored by a Mast oxidant meter continuously. Periodically, 4.4 liter samples of the chamber air are withdrawn. These samples are bubbled through KI and iodine release determined by a spectrophotometer.

Results - The first ozone decay in the dark test was conducted on January 6. The initial charge resulted in an indication of 2.30 ppm O_3, which was used as the starting concentration. The Mast output was recorded using a Honeywell Electronik 18 recorder with 5 to 50 mv adjustable full scale, which allowed following ozone concentrations greater than 1 ppm accurately. The corresponding KI bubbler reading was 2.29 ppm. Chamber

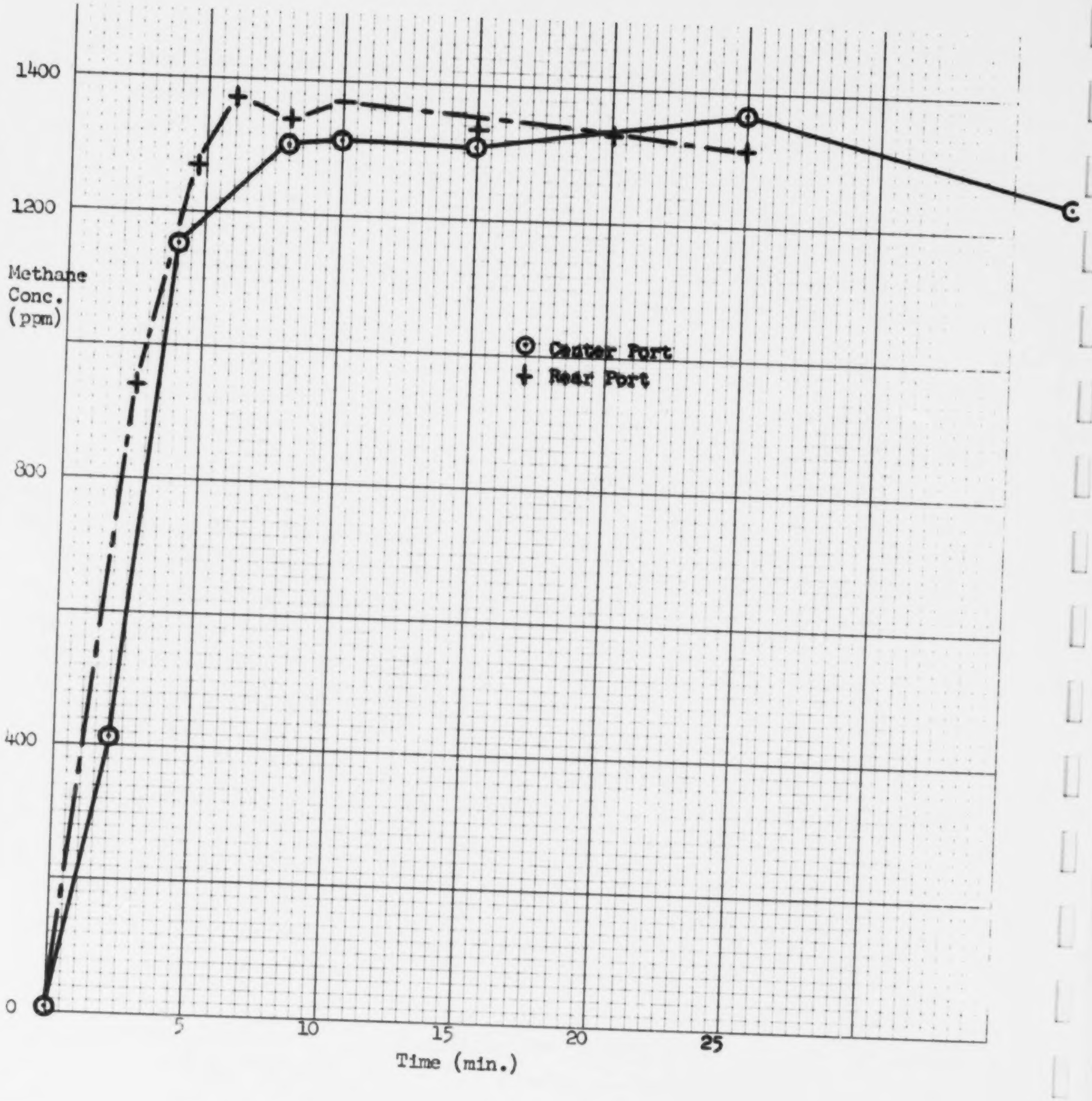


Fig. 4-6 Methane Gradient

temperature was maintained at 75 to 76°F, and pressure at 0.1 inch water, with perturbations to 0.2 inch when the bubbler samples were taken. The total hydrocarbons (excluding methane) at the start of the run were determined as 0.1 ppm, and methane was determined as 0.2 ppm.

Figure 4-7 shows the ozone concentration decay. It was observed that upon cycling each 120 minutes, the Mast did not restore itself to the same value for about 15 minutes. This accounts for the plateaus seen. Makeup gas flow averaged 1% per hour, or 16.8 liter/hour. Of this, 8.4 liter/hr is accounted for by the Mast air sampling rate. The remainder of 0.5% per hour is mostly leakage. At 1% per hour dilution rate, the apparent halflife due to dilution would be 69.3 hours, so dilution was neglected in calculating the halflife, which was done by fitting a straight line to the plot of Figure 4-7. The resulting halflife was 10.8 hours.

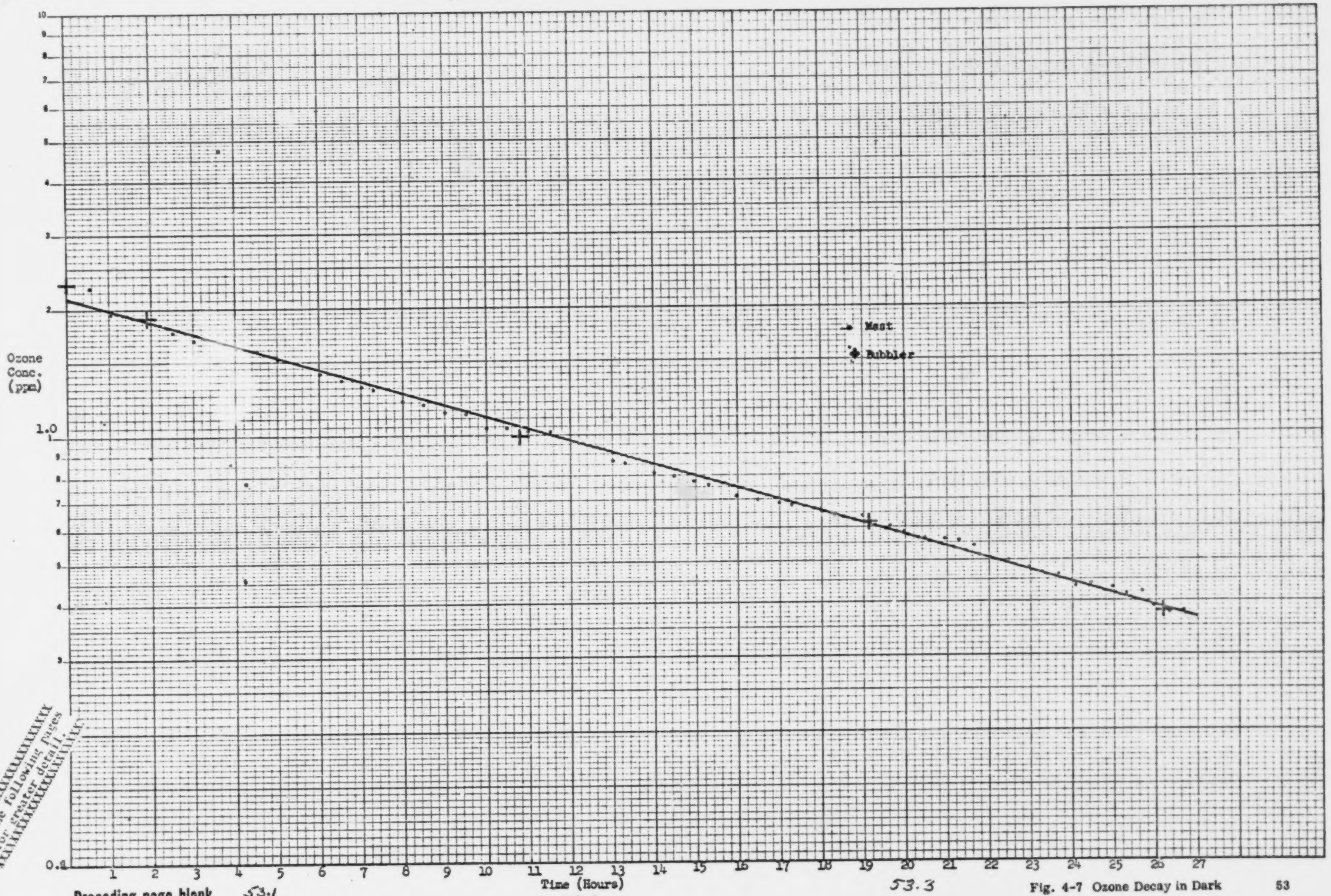
The test was repeated on January 13. For this run, the initial hydrocarbons excluding methane were determined as less than 0.2 ppm, with methane at 0.26 ± 0.05 ppm. A detailed hydrocarbon analysis was performed to determine unsaturates, and no low molecular weight unsaturates were detected (0.05 ppm lower limit of detectability).

Figure 4-8 shows the ozone concentration plot. The initial ozone charge brought the concentration to 1.86 ppm. During the first 6 hours of the test, the Mast was behaving erratically. It was debubbled and absorbing solution was pumped by hand, but the meter, in fact, corrected itself ultimately. Probably this behavior was due to a particle in the liquid check valves which worked its way through. Agreement between the Mast and KI readings was within 0.04 ppm. From the plot, a halflife of 10.3 hours is calculated.

Ozone halflife in the dark is reported at 10.6 hours.

4.6 Ozone Halflife in the Light

Method - The requirements and techniques for ozone halflife in the light determination are the same as for ozone in the dark, except that the chamber temperature is 95 ± 3°F, rather than 75°F, and that the illuminator is on during the run.



See the following pages for greater detail.

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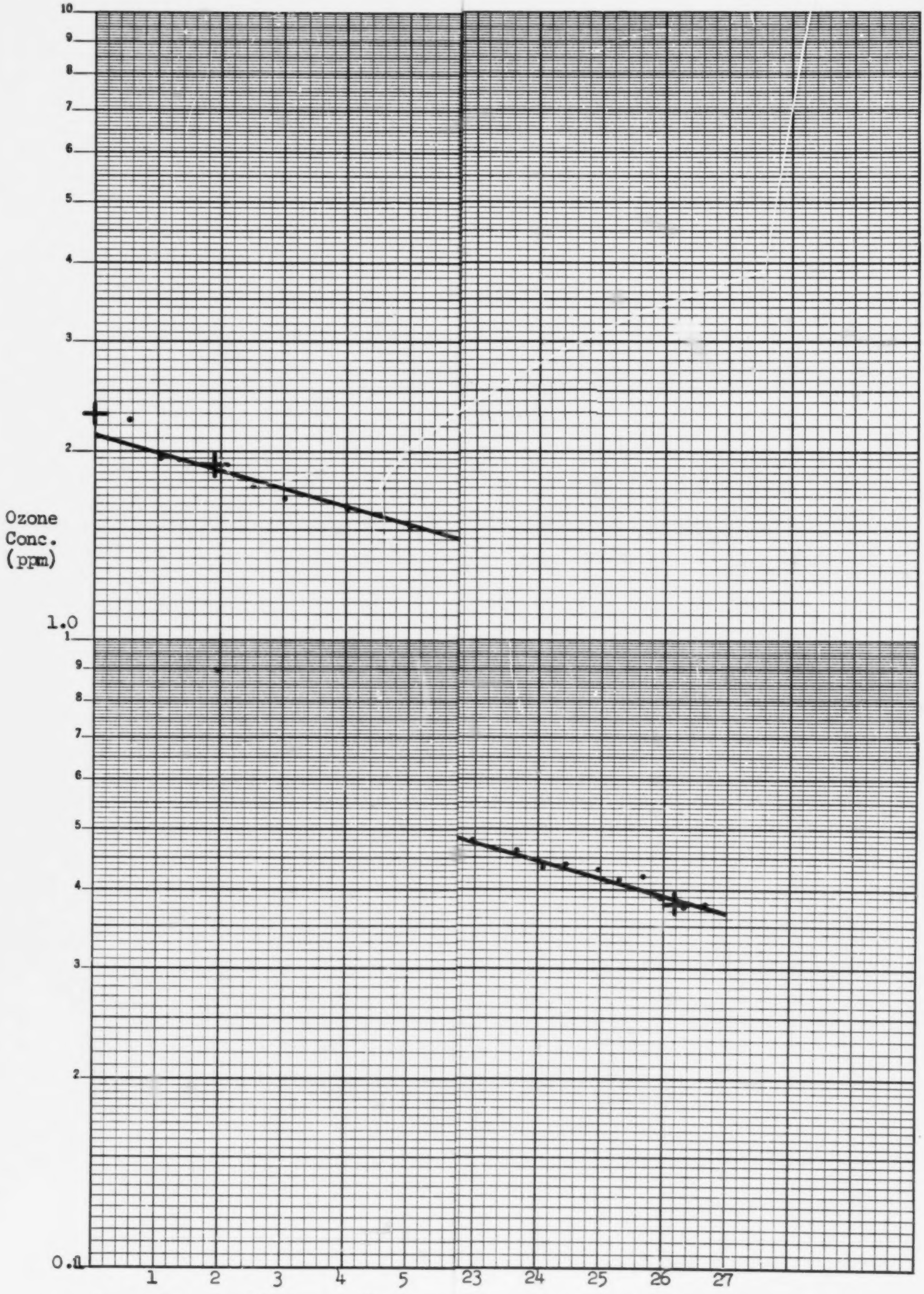
53.1

53.2

53.3

Fig. 4-7 Ozone Decay in Dark



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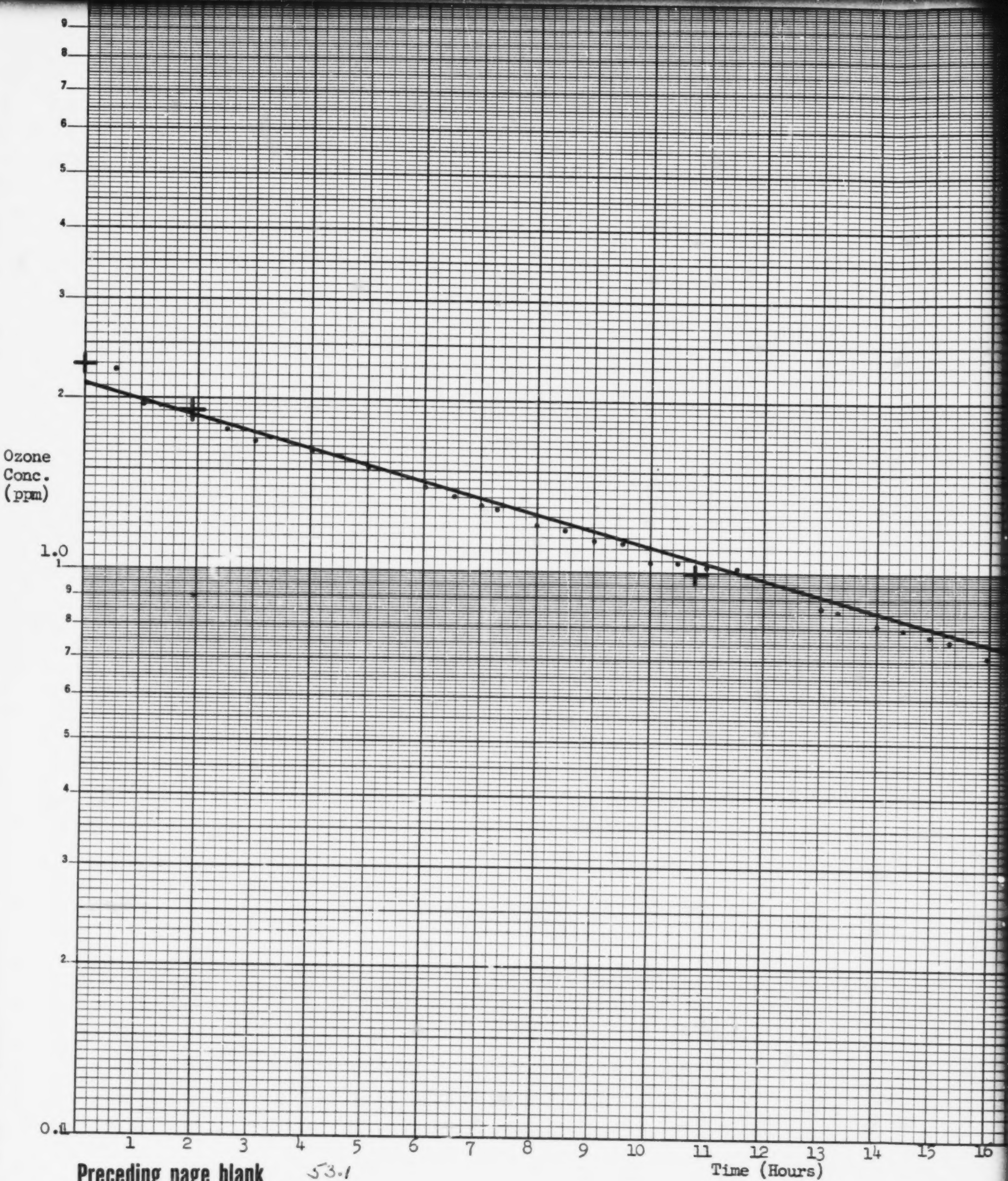
53.1

Fig. 4-7 Ozone Decay in Dark



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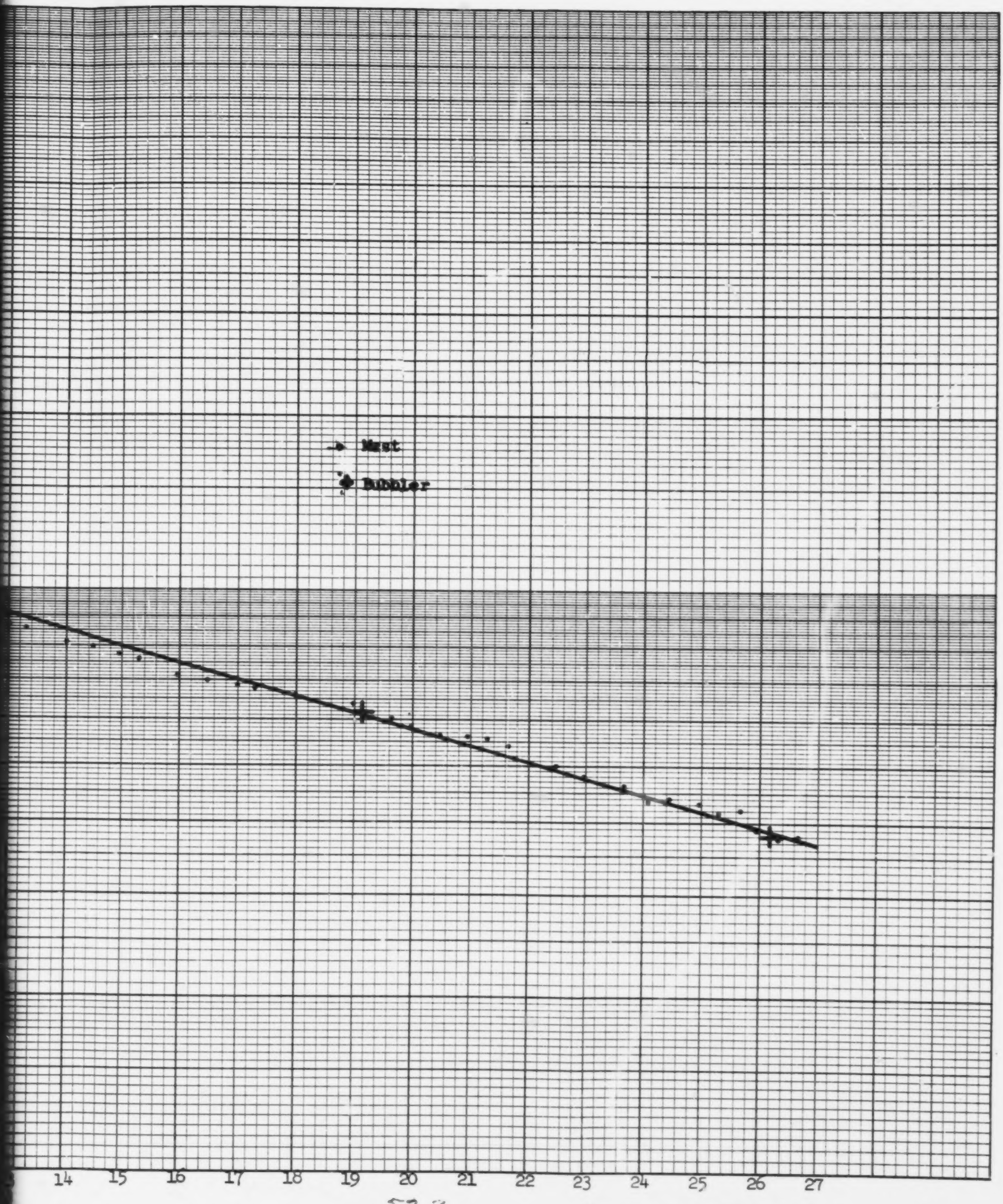

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Fig. 4-7 Ozone Decay in Dark

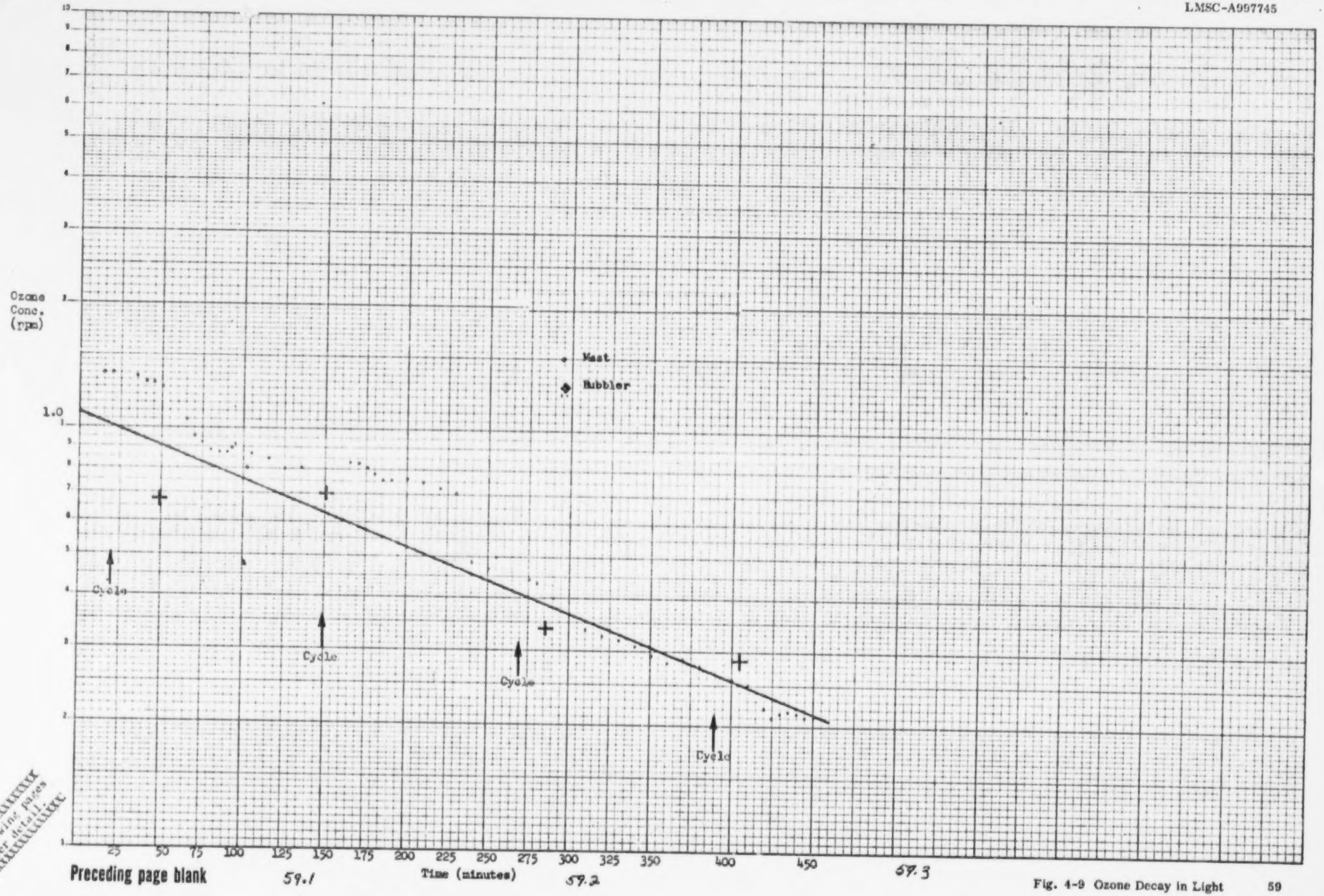

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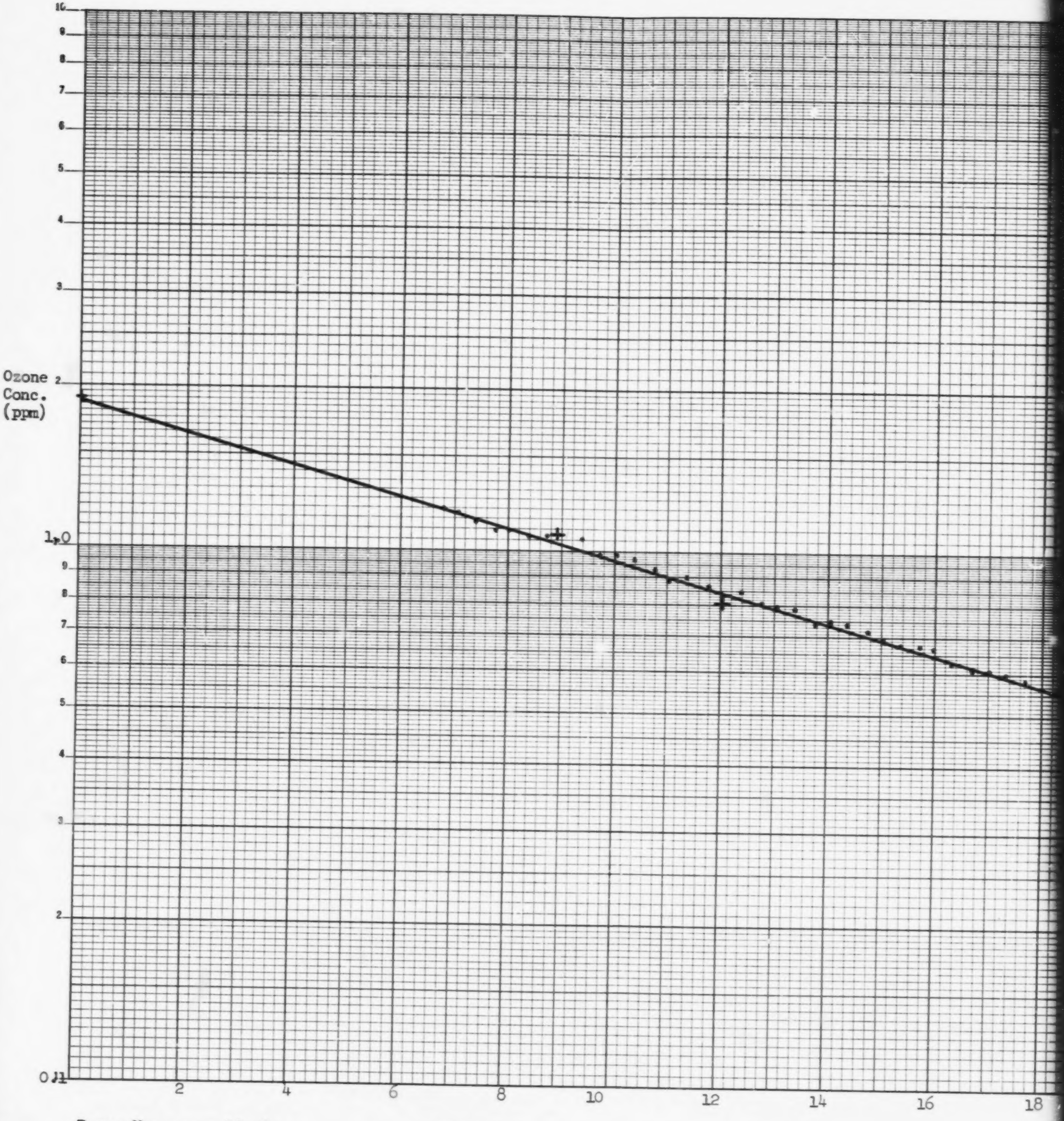
Fig. 4-9 Ozone Decay in Light



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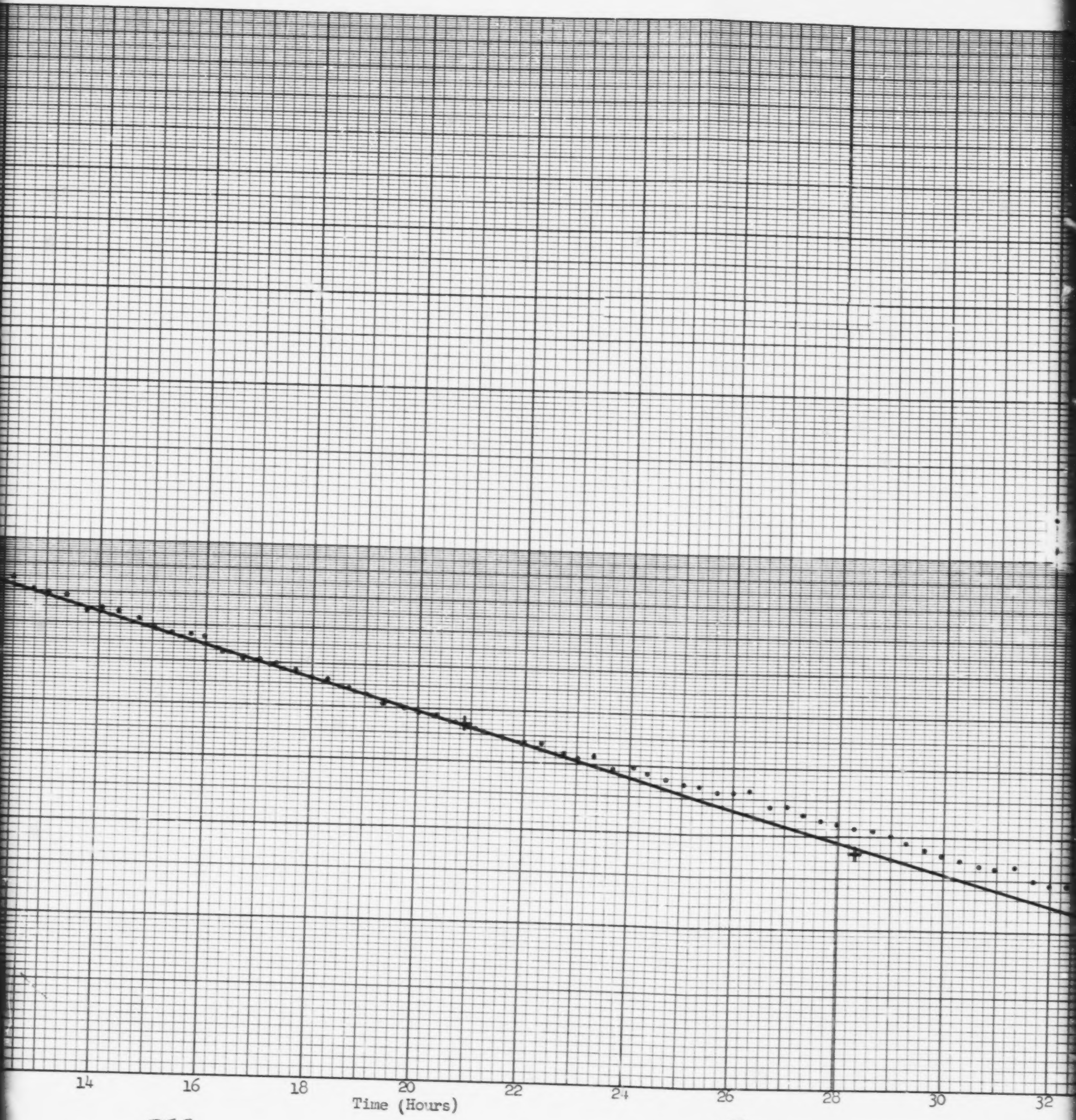

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Fig. 4

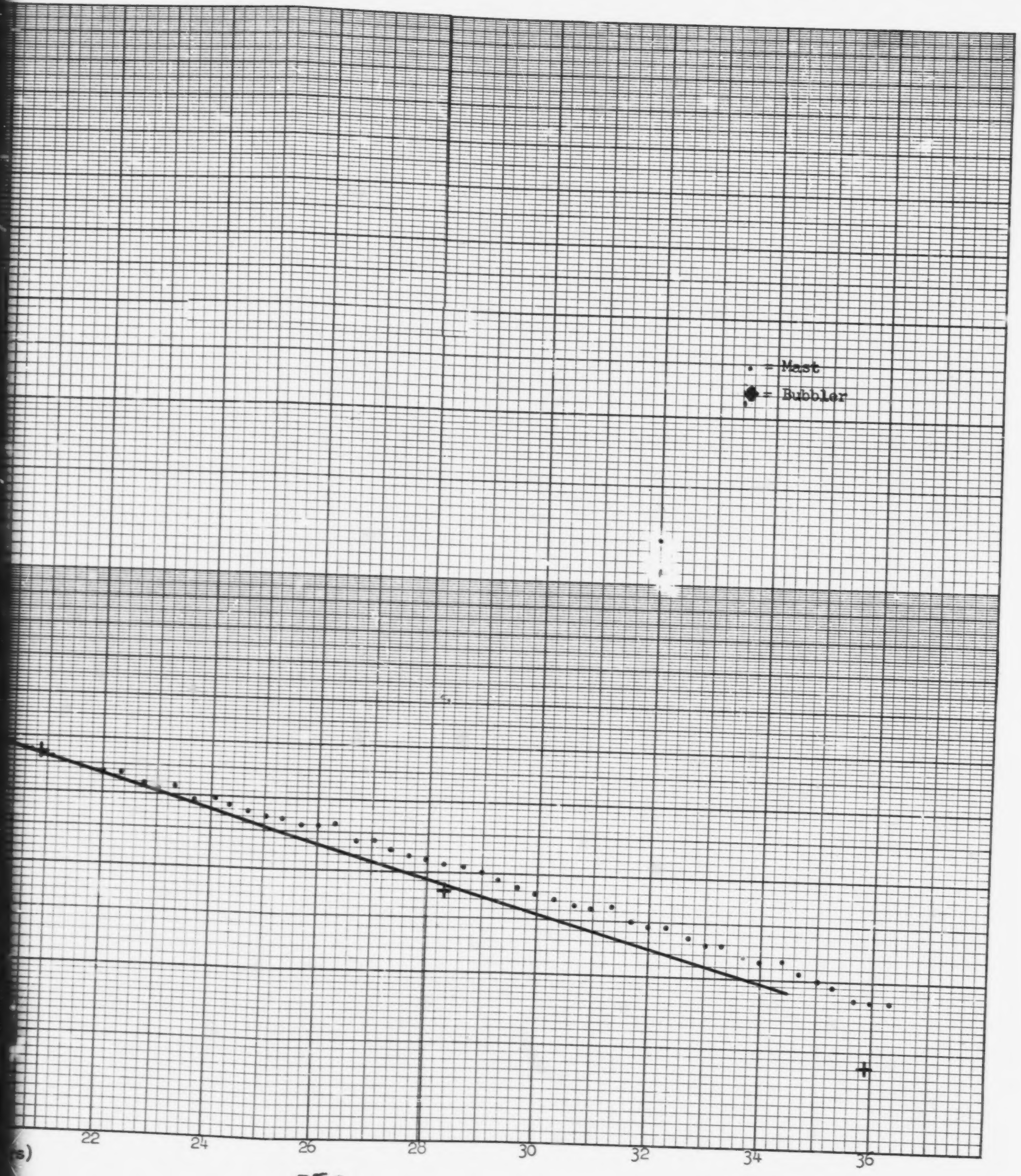

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Fig. 4-8 Ozone Decay in Dark

Results - Ozone was charged and the initial concentration measured at 1.04 ppm by the Mast and 1.10 by KI bubbler. Total hydrocarbons (excluding methane) were about 0.1 ppm, and methane was about 0.15 ppm. The illuminator was turned on and maintained at 6400 to 6500 watt.

Figure 4-9 shows the Mast and bubbler values for ozone concentrations. From the slope of the straight line fit, a value of 3.20 hours is calculated for the halflife. After the run, the Mast instrument was modified to attempt to reduce the erratic behavior noted at each cycle. The modification was to remove the liquid recycle features. Subsequent operation has been smoother with fewer bubbles in the liquid and a shorter cycle disturbance.

The repeat of the ozone halflife was conducted on January 20. Total hydrocarbons (excluding methane) were 0.1 ppm. The initial ozone was 0.88 ppm by the Mast. Ozone concentration as read by the Mast meter followed a smooth downward trend, as shown in Figure 4-10. The manual bubbler technique was consistantly lower than the Mast, but gave the same slope. Halflife is taken from the Mast values as 3.75 hours.

The average of these two values, 3.5 hours, is reported as the ozone halflife in the light.

4.7 Dummy Run

Method - The objectives of the dummy run were (1) to study thermal oxidation of NO to NO_2 in the absence of light; (2) to provide a dress rehearsal for mechanics of sampling and analysis; and (3) to become familiar with analysis methodology responses to sample gas mixtures. For the dummy run, the chamber is charged by purging with ultra zero air (less than 0.1 ppm total hydrocarbons) through the humidifier. Dew point is then adjusted by purging in ultra zero air in the dry state as received in the gas tank. The chamber is brought to temperature. Propylene is charged to the chamber, to bring it to 3.0 ppm. Then NO is charged to attain 1.5 ppm. During the run, temperature is maintained at 95 ± 3°F, pressure at 0.10 ± 0.05 inch water, and relative humidity at 25 ± 5% (54 ± 5°F dew point).

Results - The initial total hydrocarbon content of the chamber was about 0.1 ppm. Total hydrocarbons excluding methane were 0.08 ppm, and methane was 0.02 ppm. The chamber was charged with propylene using a stock cylinder of 1400 ppm propylene in ultra zero nitrogen (less than 0.1 ppm total hydrocarbons).

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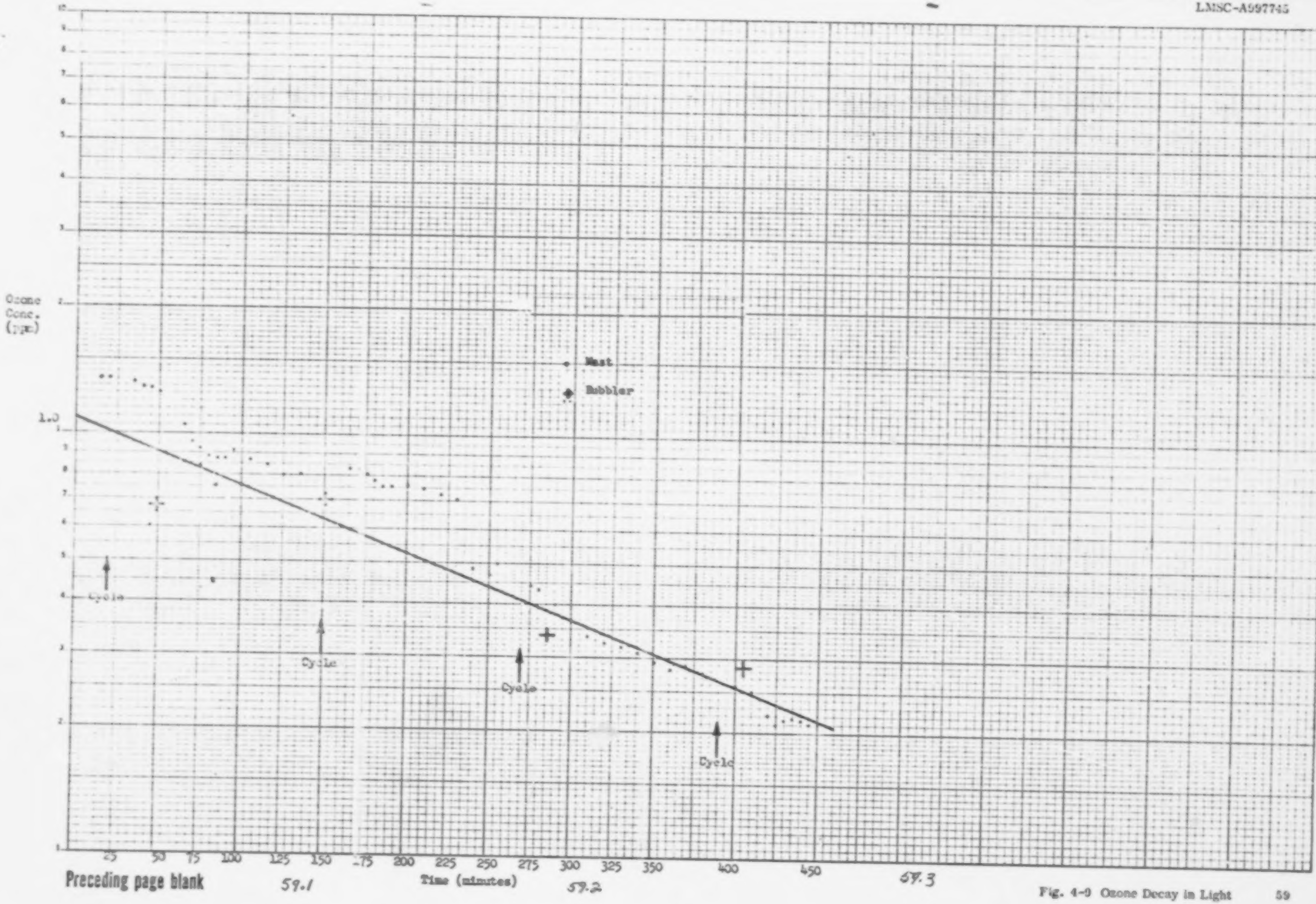

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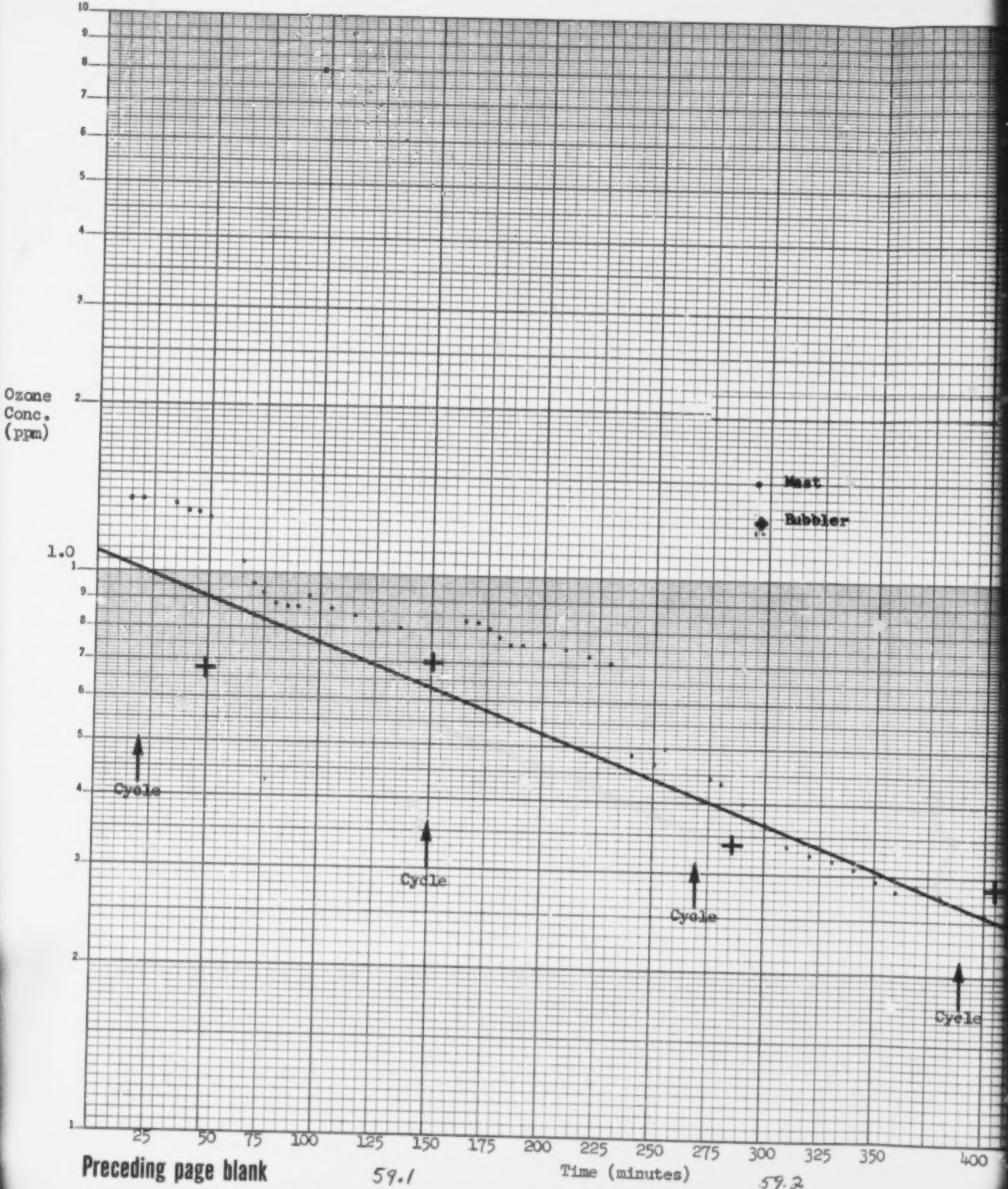
Fig. 4-9 Ozone Decay in Light



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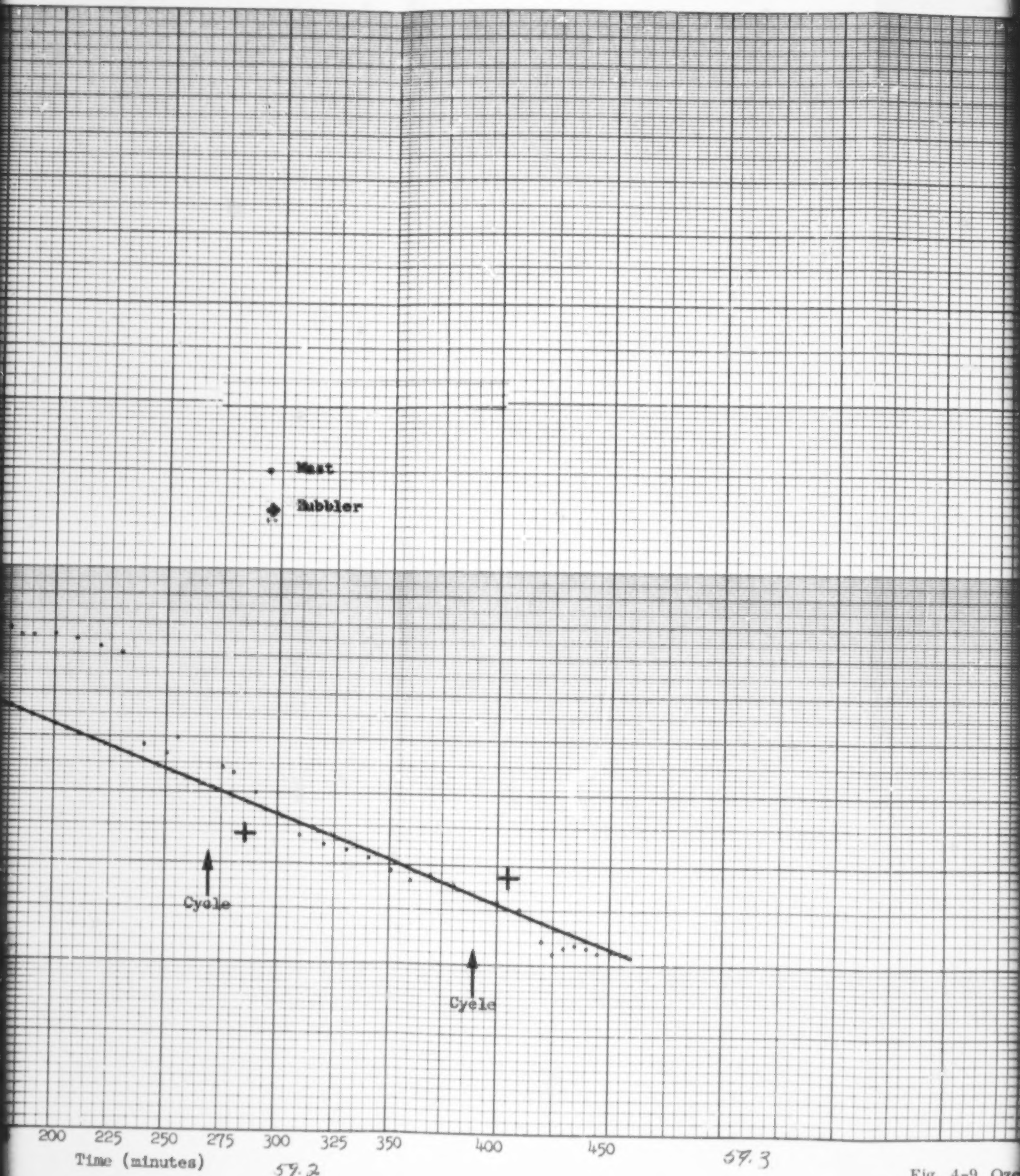

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Fig. 4-9 Ozo

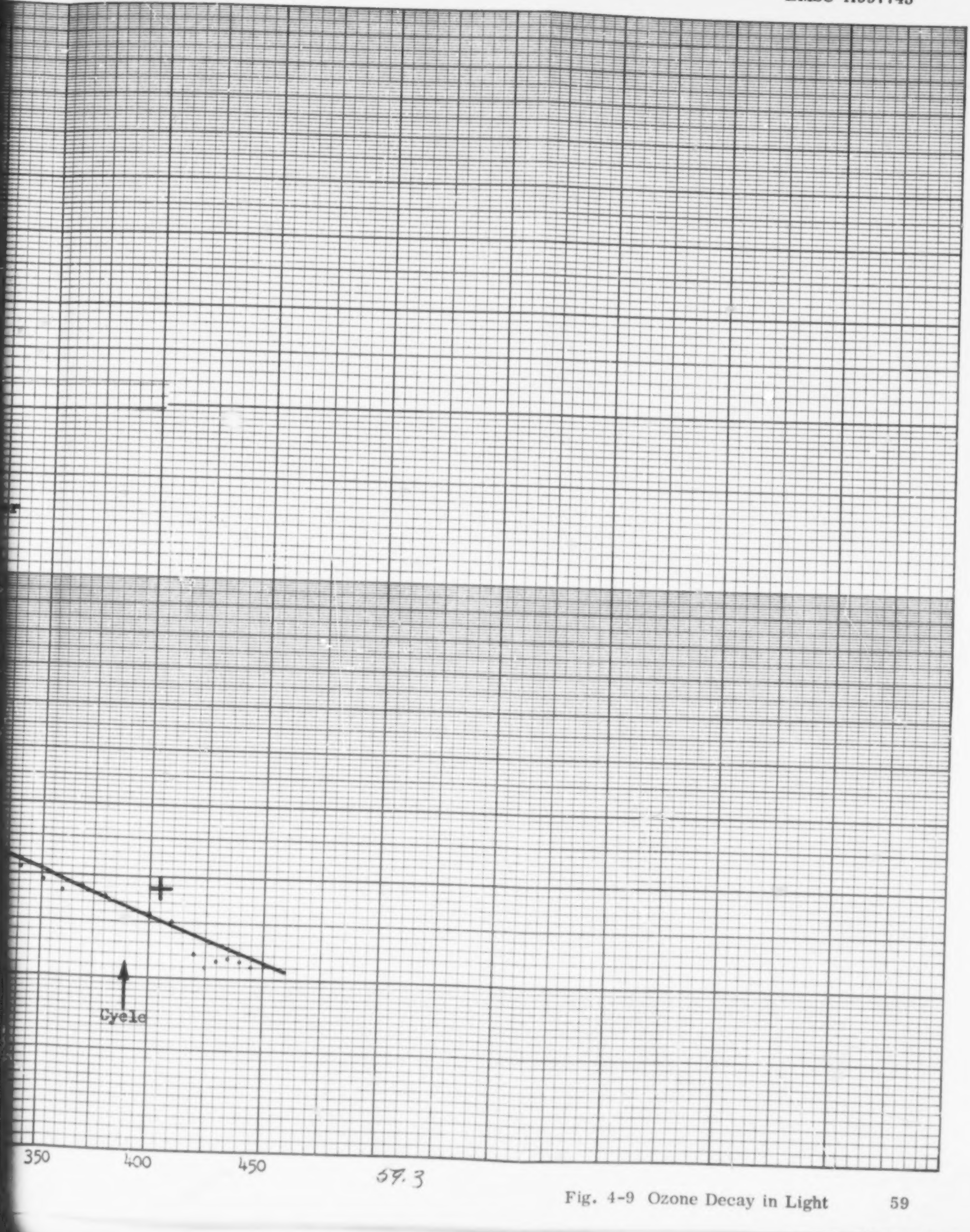

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Fig. 4-9 Ozone Decay in Light

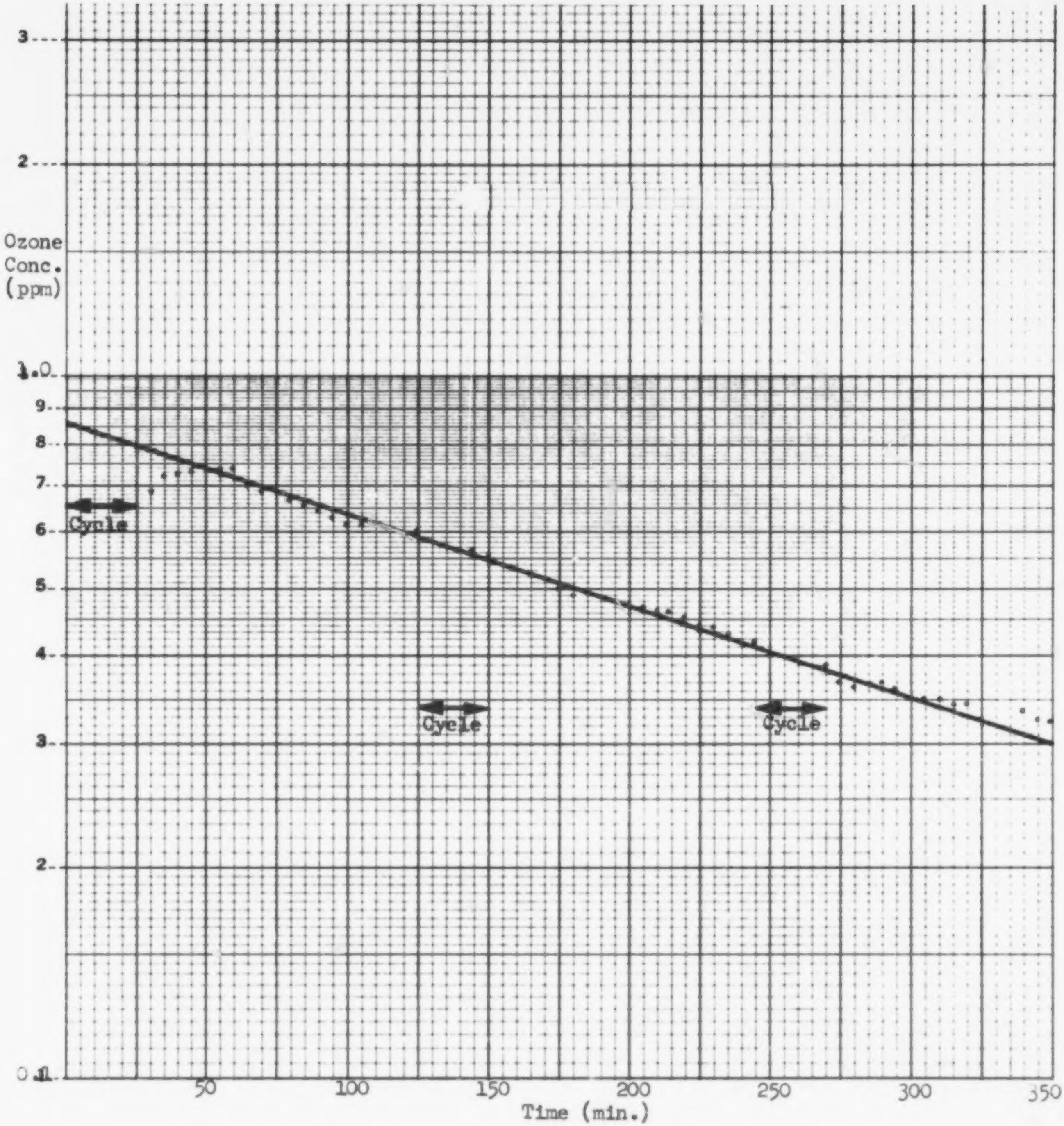

Fig. 4-10 Ozone Decay in Light

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A transfer cylinder is pressurized to 120 psig, placed on the inlet manifold and bled into the chamber. A similar technique is used for charging NO. The stock cylinder contains 685 ppm NO in nitrogen. Figure 4-11 shows the results of the dummy run.

NO_2 increased steadily during the run. Subsequent dummy runs confirmed that the apparent NO_x increase in this run was not real, so the data was analyzed by assuming a constant NO_x concentration of 1.50 ppm. NO was found by subtracting the recorded NO_2 content from 1.5. The plot of reciprocal NO concentration vs time is given in Figure 4-12. The solid line is a fit to the data. The dashed line shows the expected thermal oxidation, at a rate constant k' of 2.15×10^{-19} cc/mole sec, (3.22×10^{-4} per ppm-minute). (Ref. 4-5).

Bubbler samples were taken for formaldehyde and oxidant. The formaldehyde samples showed the same response as the blank, i.e, no detectable formaldehyde at 0.05 ppm lower limit of detectability (LLD). The oxidant sample showed 0.14 ppm oxidant at the time the Mast meter showed 0.07 ppm. (This is a larger disparity than shown during calibration, or at the higher oxidant levels observed in the ozone halflife determinations, or during the photochemical runs.)

Analyses for PAN showed no detectable PAN at 0.02 ppm LLD. The acetaldehyde samples could not be interpreted due to water interference. The column temperature has been raised to avoid this problem in the future. Dew point ranged from 54 to 58°F.

Propylene concentration was based on one determination per sample, and showed about 8% precision. A downward drift corresponding to the dilution by makeup gas was observed. The table below shows the gas balance.

Dilution Gas Added

Source	Calculated Amount
Continuous Sampling	132 liter
Bubblers	18.7
Gas Grab Samples	14.5
Dew Pointer	12.0
Leakage at 0.1 inch water	36.3
Total Calculated	203.5
Observed Inflow	209

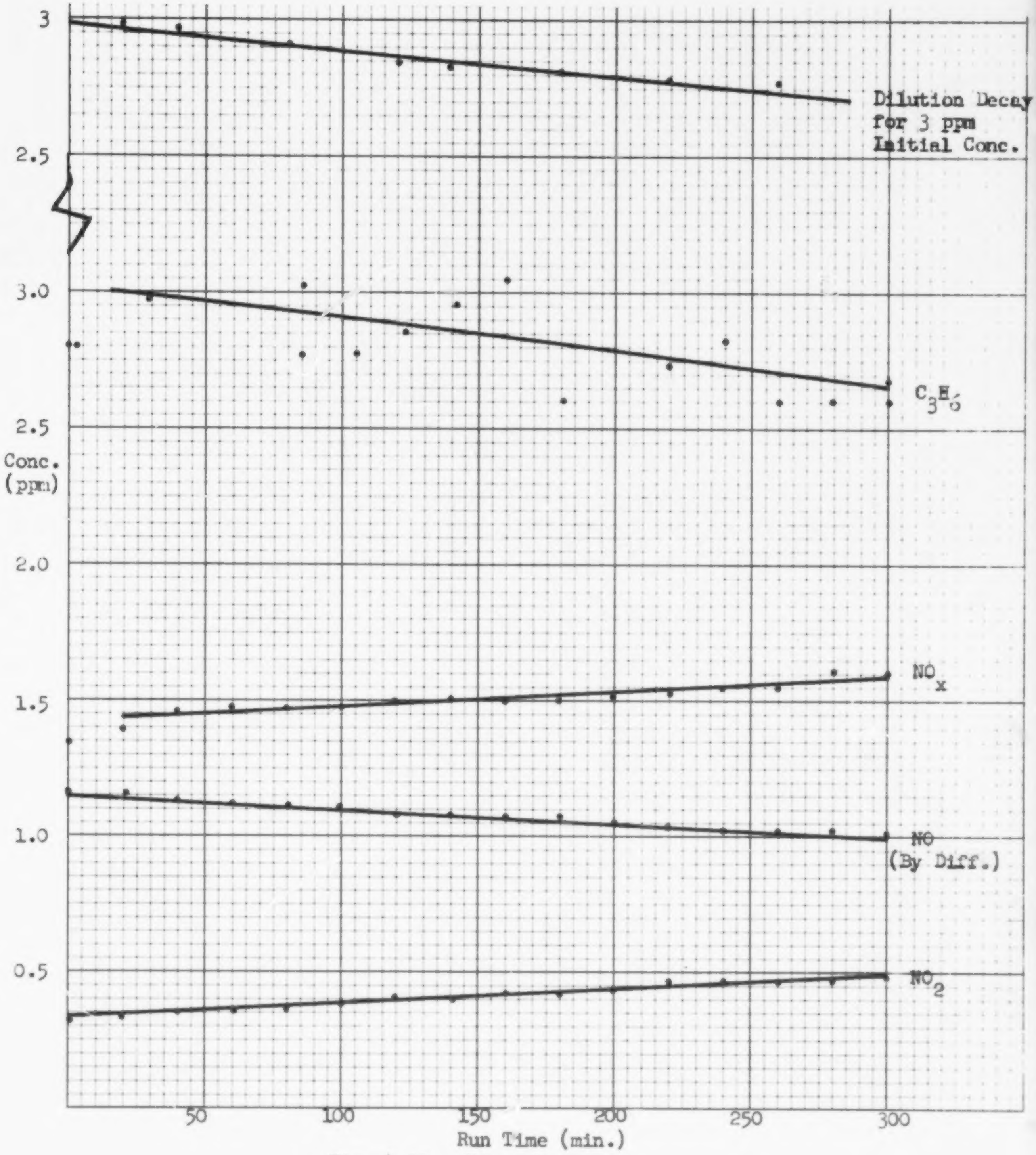

Fig. 4-11 Dummy Run

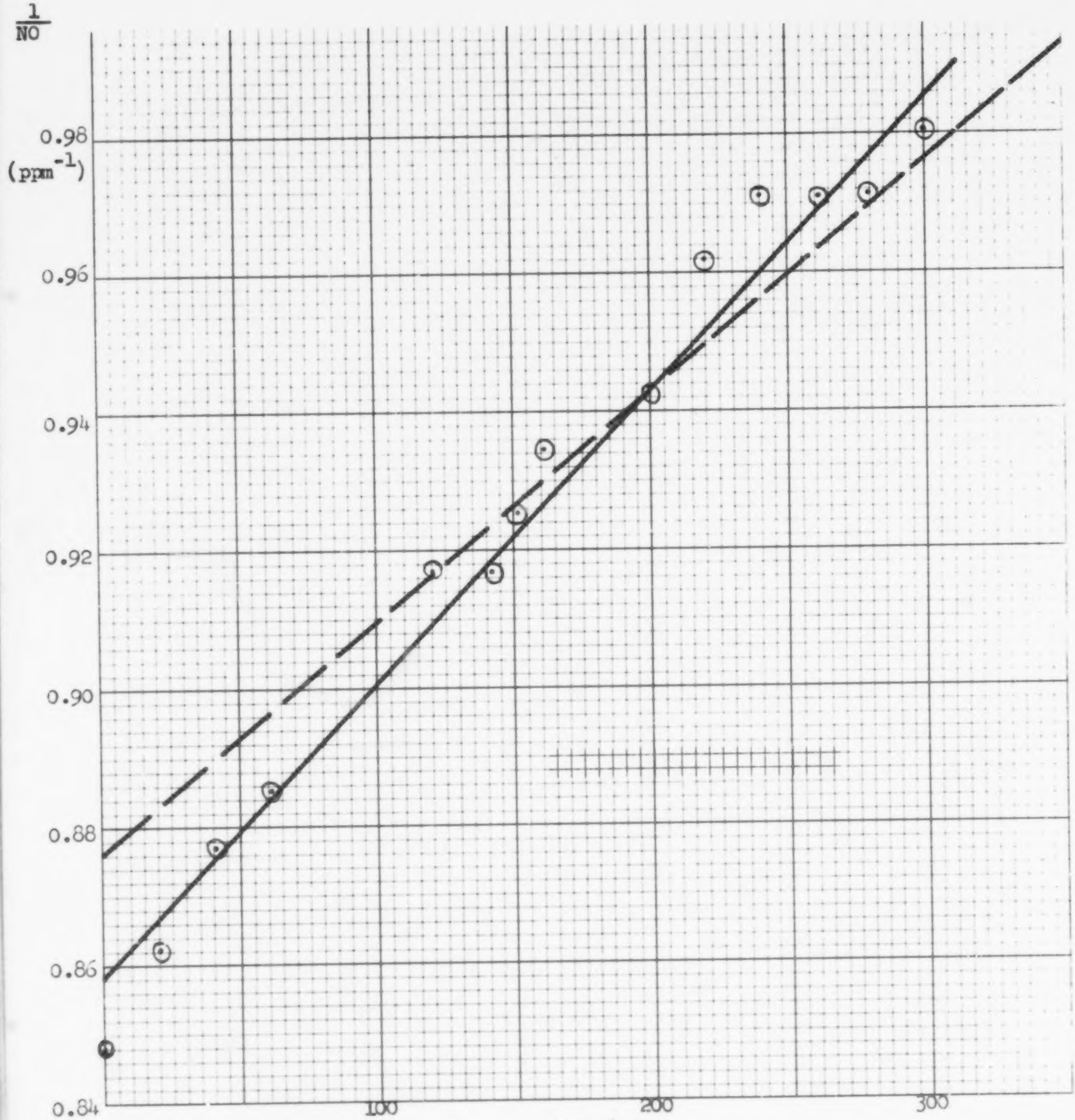

Fig. 4-12 1/NO vs Time

The initial NO_2 content obtained was 0.34 ppm, which was deemed excessively high. Even with introduction of the NO at about 700 ppm into air rather rapid thermal oxidation to NO_2 occurs. In the reaction system:

$$2NO + O_2 \rightarrow 2NO_2$$

$$\frac{-d(NO)}{dt} = \left[2K(O_2)\right] (NO)^2 = k'(NO)^2$$

$k' = 2.15 \times 10^{-19}$ (cc/mole)/sec for atmospheric oxygen content and room temperature (Ref. 4-5). The initial halflife for NO is given by:

$$t_{\frac{1}{2}} = \frac{1}{k'(NO)}$$

For 700 ppm NO, the initial halflife is 4.4 minutes, showing that rapid dilution is important to avoid high initial NO_2 content. Introduction of NO was subsequently accomplished by use of a 1/4" stainless tube inserted directly into the side stream mixer. The addition manifold is flushed at about 10 l/min of ultra-zero nitrogen for about two minutes, then the NO-in-nitrogen charge cylinder opened to the manifold with the mixer on, and flushed into the chamber for an additional 4-5 minutes. Using this technique, the following initial NO_x and NO_2 concentrations are obtained:

Experiment Date	NO_x (= NO + NO_2)	NO_2	NO_2/NO_x as percent
2-10-72	1.65 ppm	0.18 ppm	10.9
2-17-72	1.63	0.20	12.2
3-1-72	1.54	0.15	9.8
3-8-72	1.45	0.09	6.2

These results compare favorably with those obtained by other using direct syringe introduction of NO into a mixer, or by use of a 4-way gas chromatograph sampling loop valve.

The first dummy run indicated that there was some apparent uncertainty involved in measurement of NO_x, as NO_x concentration is expected to essentially follow the chamber concentration-dilution curve, except for possible chamber absorption effects. Consequently, the methodology and technique for NO_x and

NO_2 measurement was re-examined, and the instrumentation recalibrated. Two additional runs were then performed, in which only NO_x was charged. Figure 4-13 shows the results. For these, NO_x concentration was essentially as expected, and followed the dilution curve.

Another analysis of NO thermal oxidation was performed using the 2/10/72 data set, and the results are shown by Figure 4-14. In this run, the rate constant was determined as 4.0×10^{-4} per ppm-minute, or about 23% deviation from the accepted value.

4.8 Illumination Intensity and Spectral Distribution

Two independent photometric methods were used to determine the intensity and spectral distribution at the smog chamber front and back faces, on the outside of the chamber. The simple method makes use of a commercial ultraviolet intensity meter (Ultra-Violet Products, Inc., Model J-221), which has a peak response at 354 nm and is sensitive to the 300-400 nm range and to the infrared. Two readings are required to determine uv intensity; the first reading is taken without any filters and the second reading is taken with a filter which blocks all light below 400 nm in wave length. Subtracting the second from the first gives the uv intensity. This method was used to obtain average intensity in the front and rear of the chamber.

Spectral distribution for the wavelength range of 300 to 650 nm was determined using a Beckman DK-2 spectrophotometer and a calibrated quartz-iodide source. This was accomplished for one position in front of the chamber and for one at the rear of the chamber.

Meter Method - Place illuminator and smog chamber in same position as used for photochemical reaction runs. Mark six locations to be used for intensity determination on wall behind chamber. Energize illuminator, bring to rated power, and allow to stabilize. Measure light intensity using Ultra-Violet Products, Inc. J-221 long wave uv intensity meter. To obtain a light intensity reading, the total intensity is measured. From this is subtracted the intensity measured with a filter that blocks out below 400 nm. The difference is a measure of the light intensity between 300 and 400 nm.

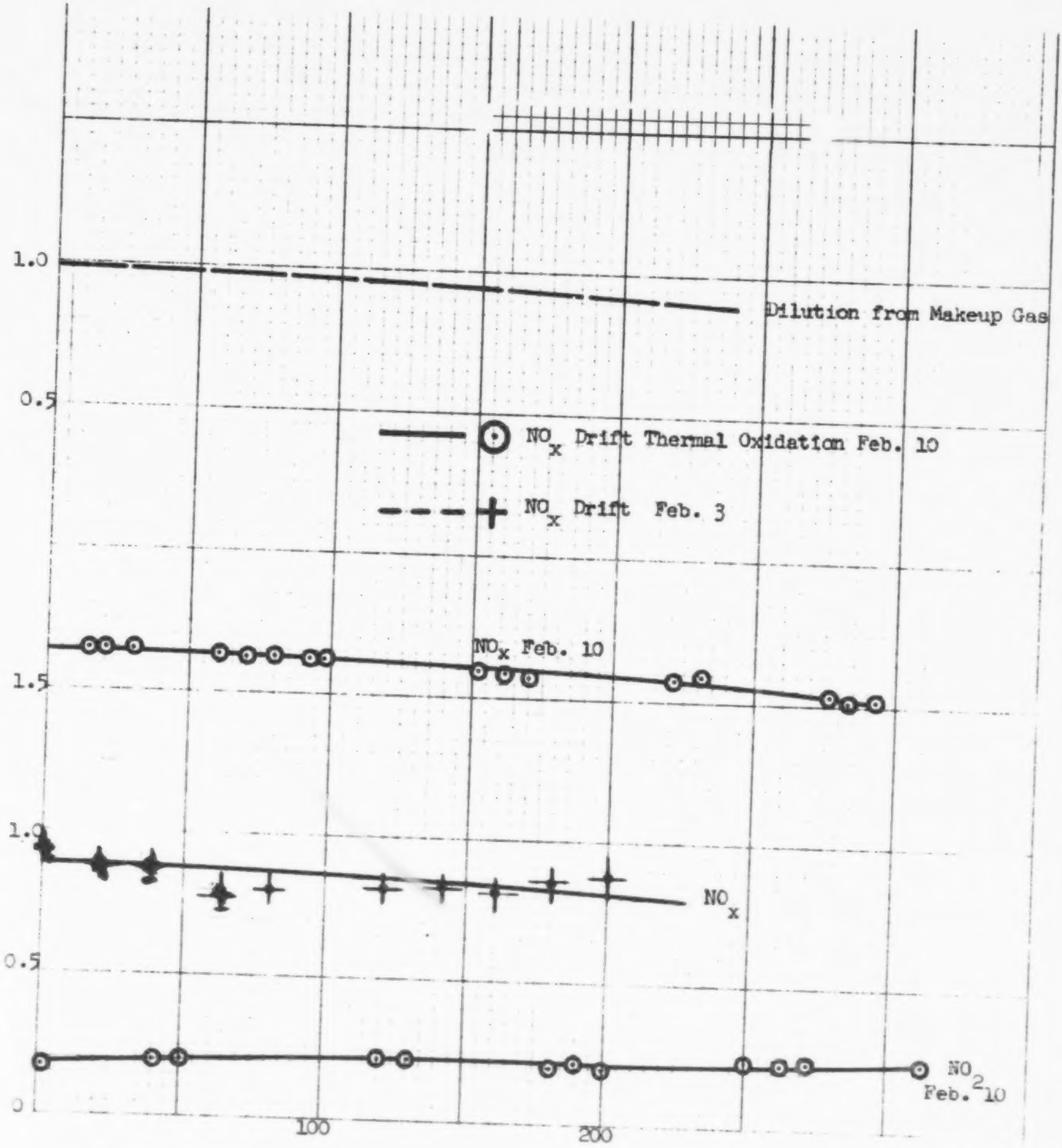

Fig. 4-13 NO$_x$ Drift Study

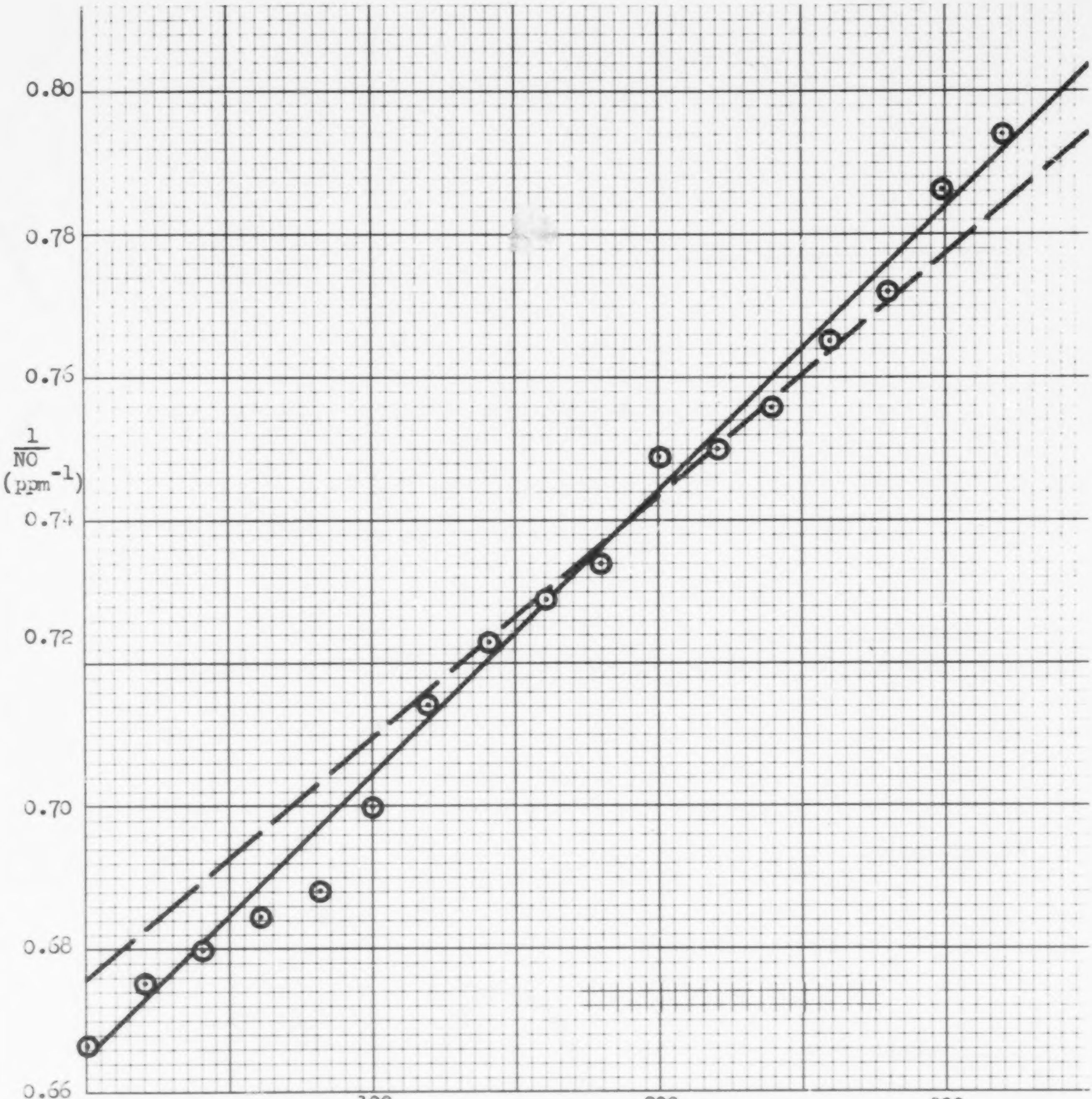

Fig. 4-14 1/NO vs. Time

Meter Results - The six measurement points selected are shown in Figure 4-15. The points are located along the diagonals of the hexagonal face and are 15 inches in from the apexes except for point 1, which had to be displaced because of sample tube shadowing. Table 4-3 gives the results for a new xenon lamp at 6500 watt power. The five foot parabolic reflector was newly aluminized, and the back collector mirror was newly plated with rhodium.

TABLE 4-3
MEASURED UV INTENSITY

Point	Intensity Front of Chamber Watt/m^2	Intensity Back of Chamber Watt/m^2
1	77.5	45.6
2	70.5	41.5
3	66.5	45.6
4	74.8	49.8
5	54.0	45.6
6	58.0	51.9
Average	67.0	46.5

The data indicate that uv intensity is reduced about 30% in tranversing both the front and rear hexagon Pyrex faces of the chamber. As the measurement meter was used without an inlet diffuser, it may have exhibited undesirably high orientation sensitivity, so that undue weight should not be given to point-by-point comparisons. Energy efficiency of the meter peaks at 365 nm, and is down to 50% relative response at 325 and 380 nm, and down to 10% at 305 and 395 nm. For situations in which the incident light spectrum does not vary appreciably, the meter provides a useful index of intensity. The accuracy of the meter is quoted by the manufacturer at ±15% at 365 nm. The precision of the intensity readings is about 10%.

Spectrophotometer Method - The radiant intensity of the collimated beam from the xenon arc lamp and reflector assembly was determined using a standard quartz iodide lamp, a reflecting mirror and spectrophotometer. The Beckman DK-2A spectrophotometer was used as a monochrometer and operated in

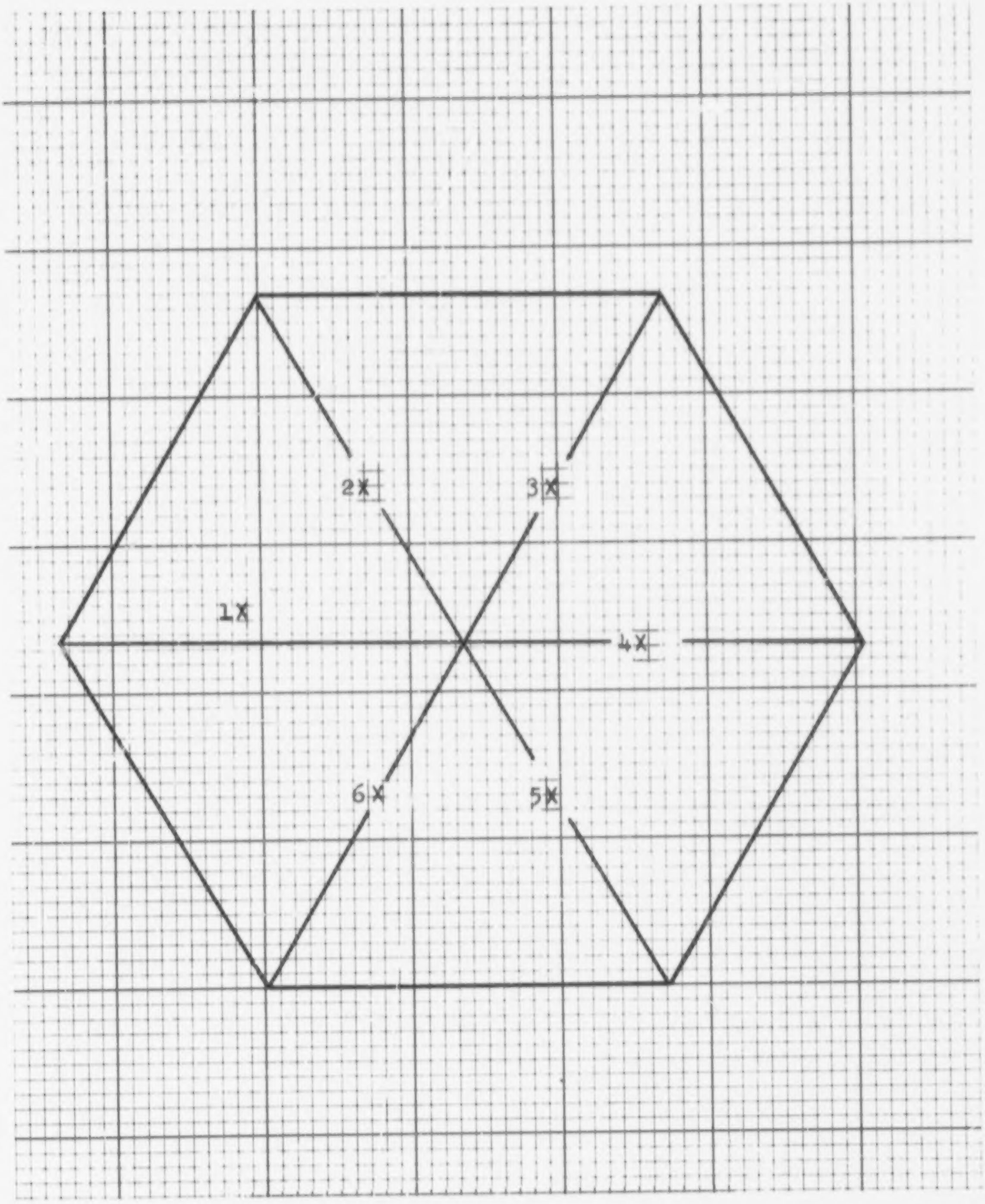

Fig. 4-15 Intensity Measurement Points

single beam mode. Since the radiant energy from the xenon lamp assembly was collimated and the radiant energy from the calibrated lamp was from a small extended line source, it was necessary to use a diffuse reflector (magnesium oxide) to reflect the source radiant energy into the spectrophotometer optical system. The field of view of the spectrophotometer was filled by both sources with the use of the diffuse reflector and the relative intensity of the two sources at the position of the magnesium oxide reflector was determined.

The magnesium oxide reflector was mounted at approximately 45 degrees to the optical axis, and to the incident collimated beam from the xenon lamp assembly, as shown in Figure 4-16. The calibrated quartz iodide lamp was located at an angle of approximately 10 degrees from the collimated xenon lamp beam. This was close enough that the diffuse reflectance of the magnesium oxide will be essentially constant.

The monochrometer alternately viewed the quartz calibrated lamp and the xenon arc lamp assembly. Calibrated neutral density screens, the electronic gain of the instrument, and slit width adjustments were used to keep the outputs on the instrument scale. The ratio of the relative radiant intensities of the two sources was determined. Then, using the calibration data for the quartz iodide lamp, the absolute spectral radiance of the xenon lamp assembly was determined.

Spectrophotometer Results - Figures 4-17 and 4-18 give the results of the front and rear of the chamber, respectively. Because of the low yield of the calibration lamp at short wavelengths, the absolute values shown must be considered as preliminary at this time. Additional effort using a lock-in amplifier with a wide dynamic range and a photomultiplier tube-power supply combination with greater stability is planned. The main features of the spectrum are well reproduced, as can be seen by comparison to Figure 4-19, which shows manufacturers data for the spectral distribution of the lamp itself.

The relative distribution in the 300 to 400 nm region is given in Figure 4-20, as percent of total in that region in each 10 nm band. The absorption effect of the Pyrex faces is shown in the lower relative energy content below about 315 nm. For reference, the Mount Wilson data is also shown on this plot. The data used was October 16, 1965 at 12:15 PM (Ref. 4-6).

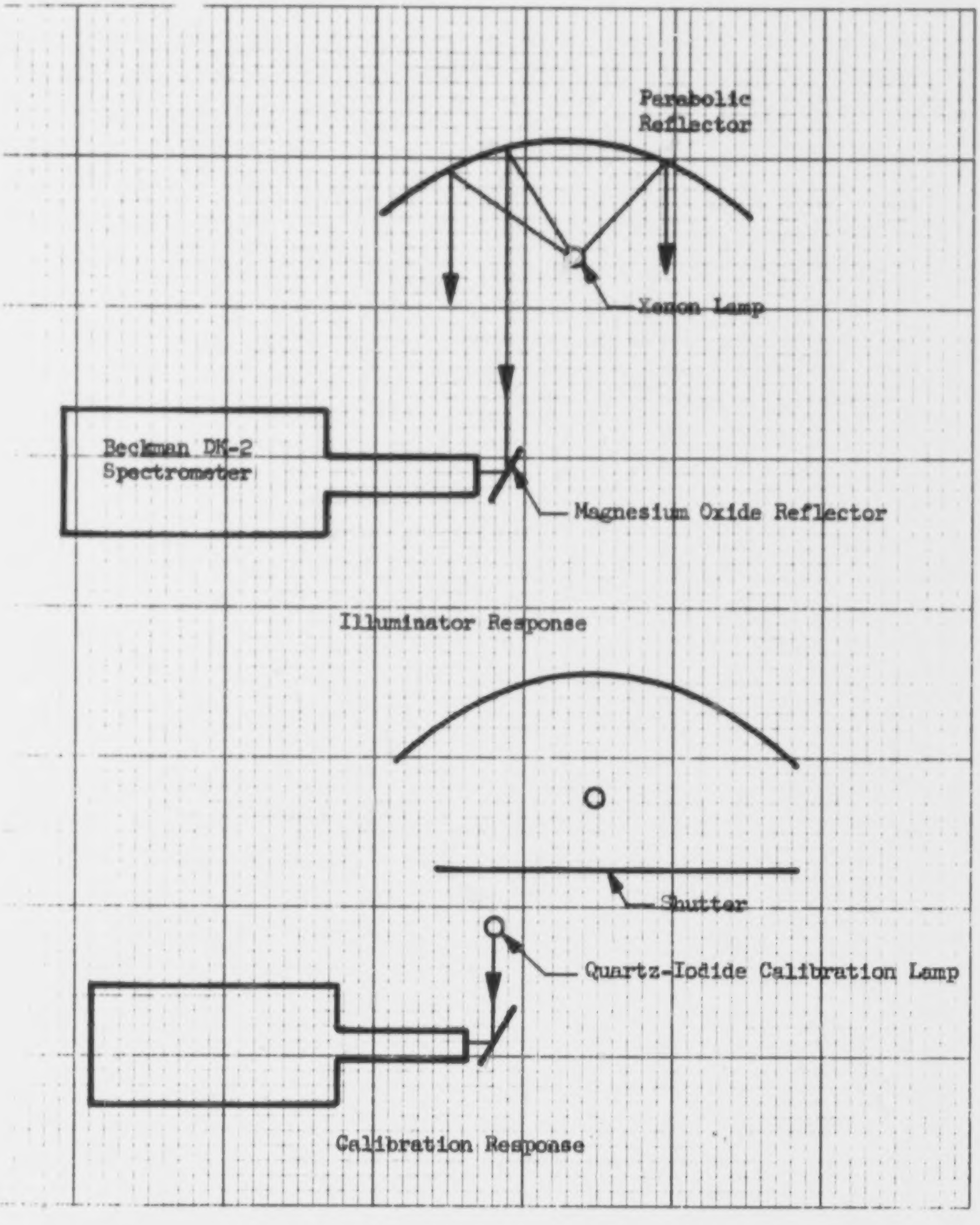
Parabolic Reflector
Xenon Lamp
Beckman DK-2 Spectrometer
Magnesium Oxide Reflector
Illuminator Response
Shutter
Quartz-Iodide Calibration Lamp
Calibration Response

Fig. 4-16 Spectro Radiometry Arrangement

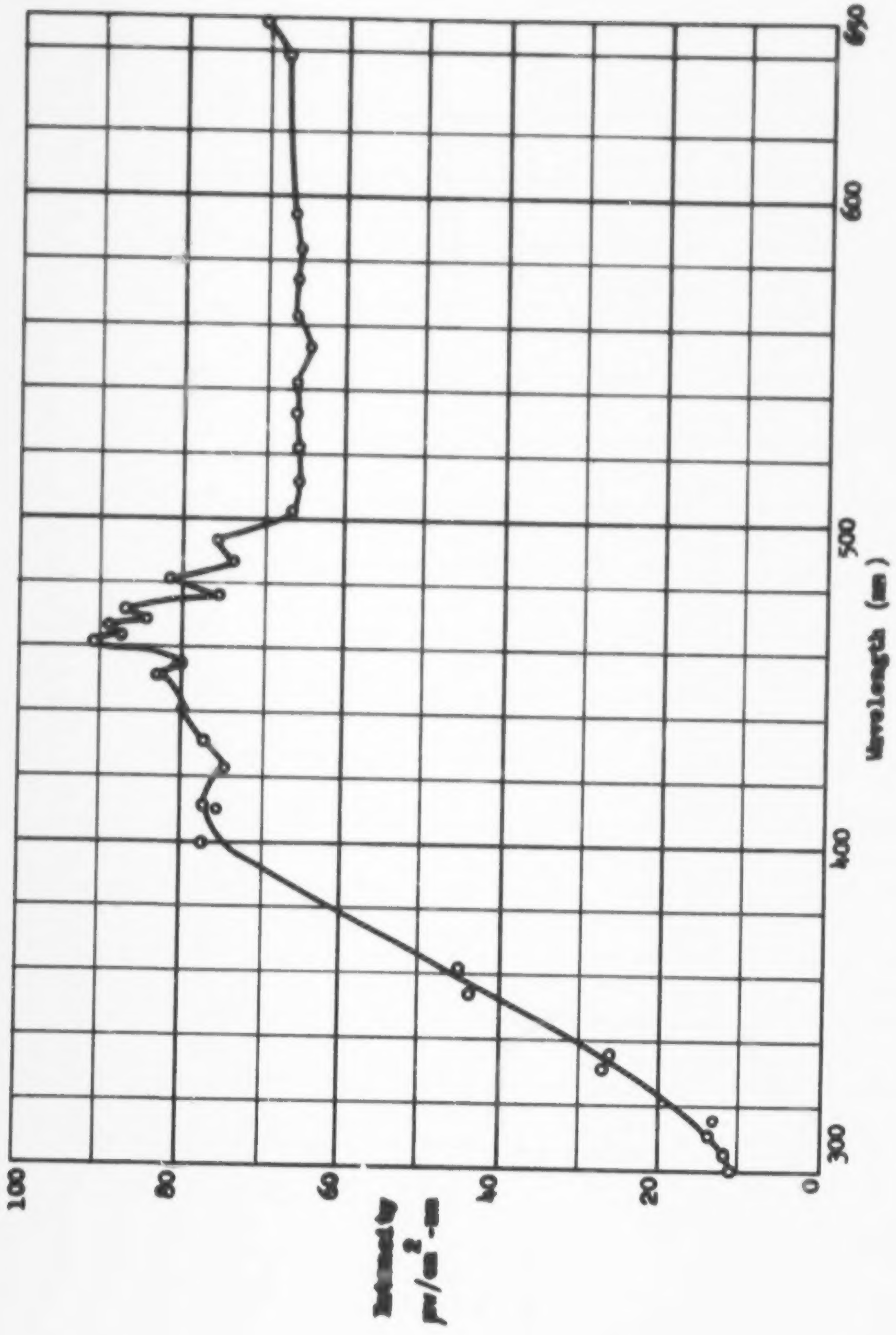

Fig. 4-17 Spectral Distribution at Chamber Front Face

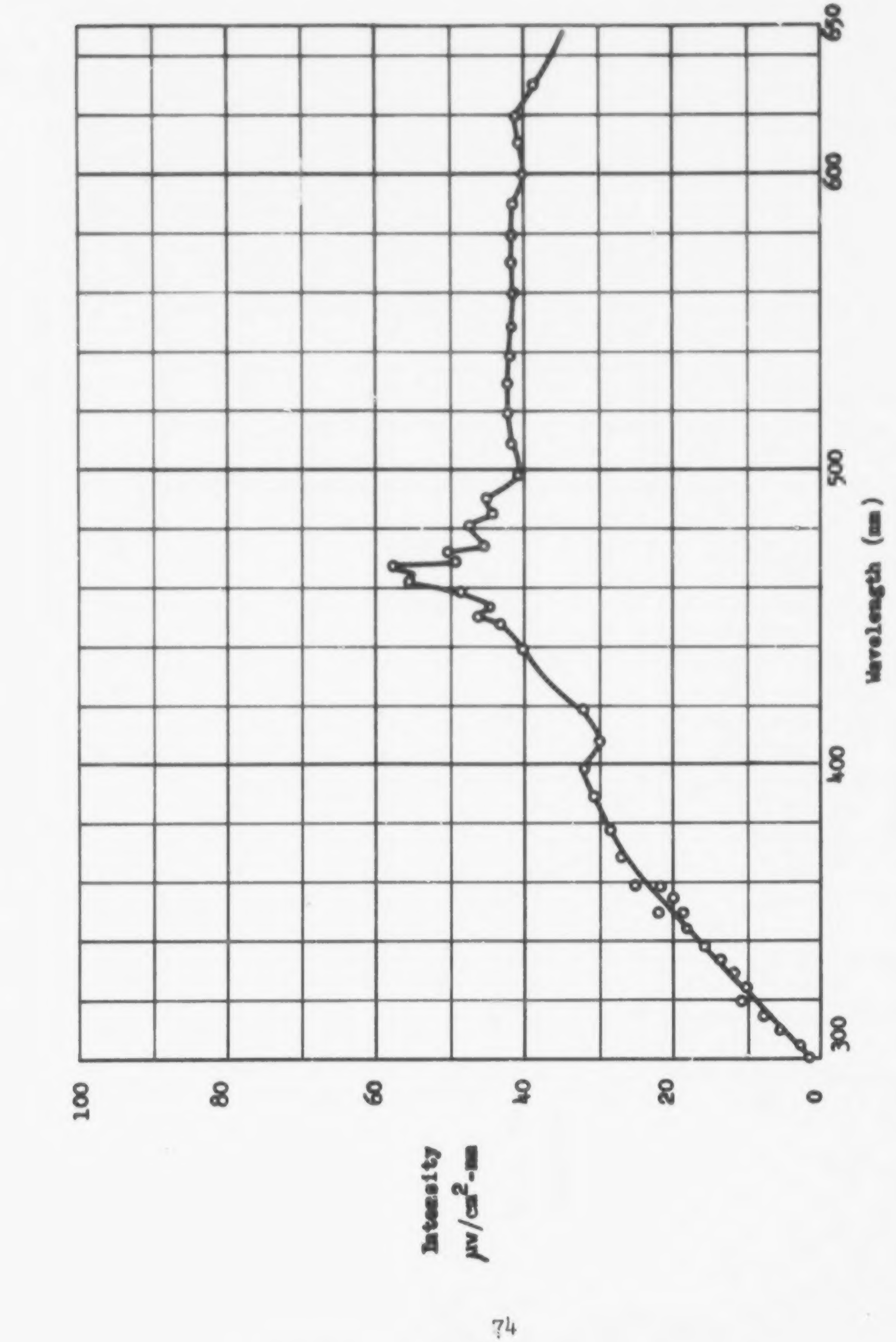

Fig. 4-18 Spectral Distribution Emerging from Chamber Rear Face

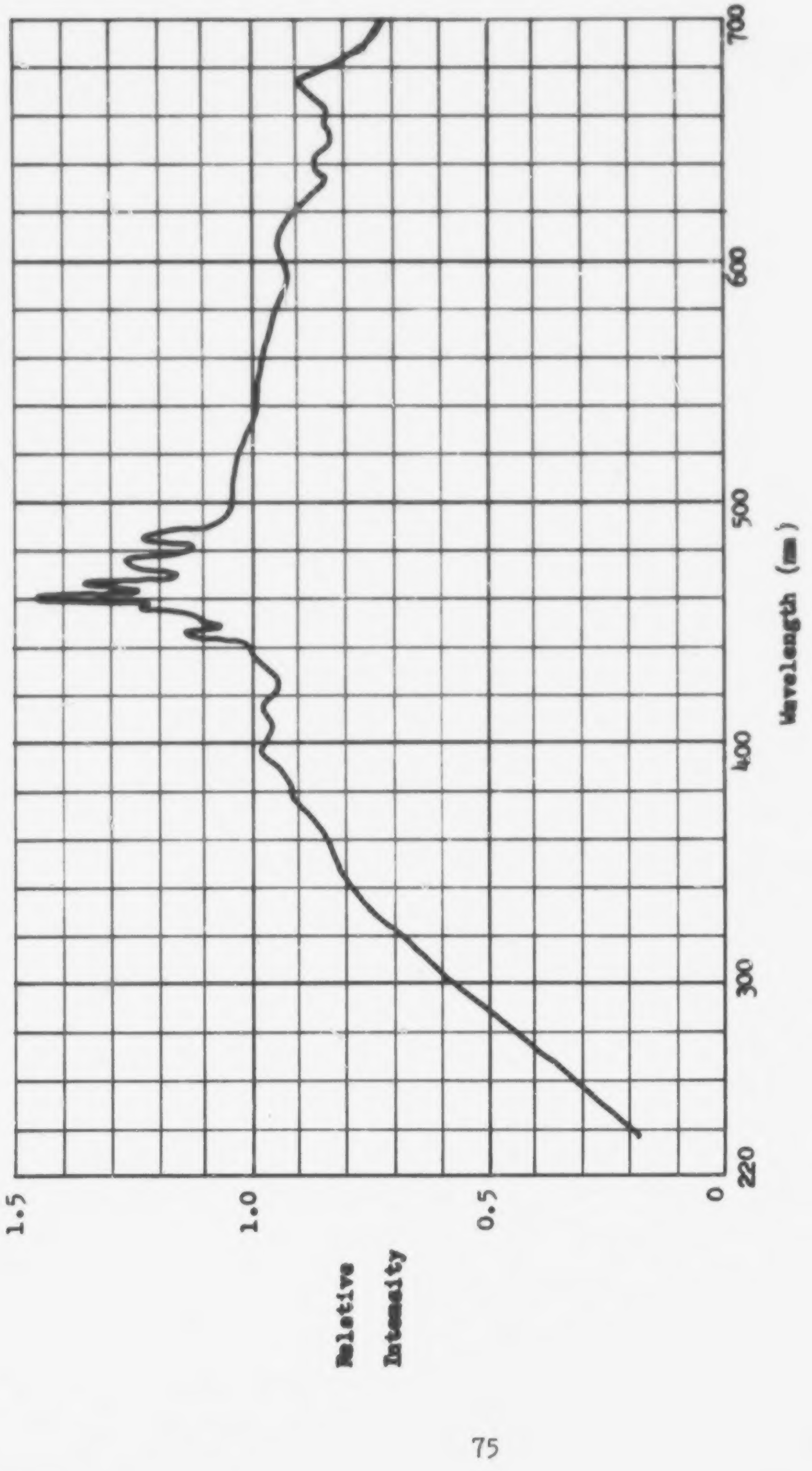

Fig. 4-19 Relative Spectral Distribution Osram
6500 Watt Xenon Lamp

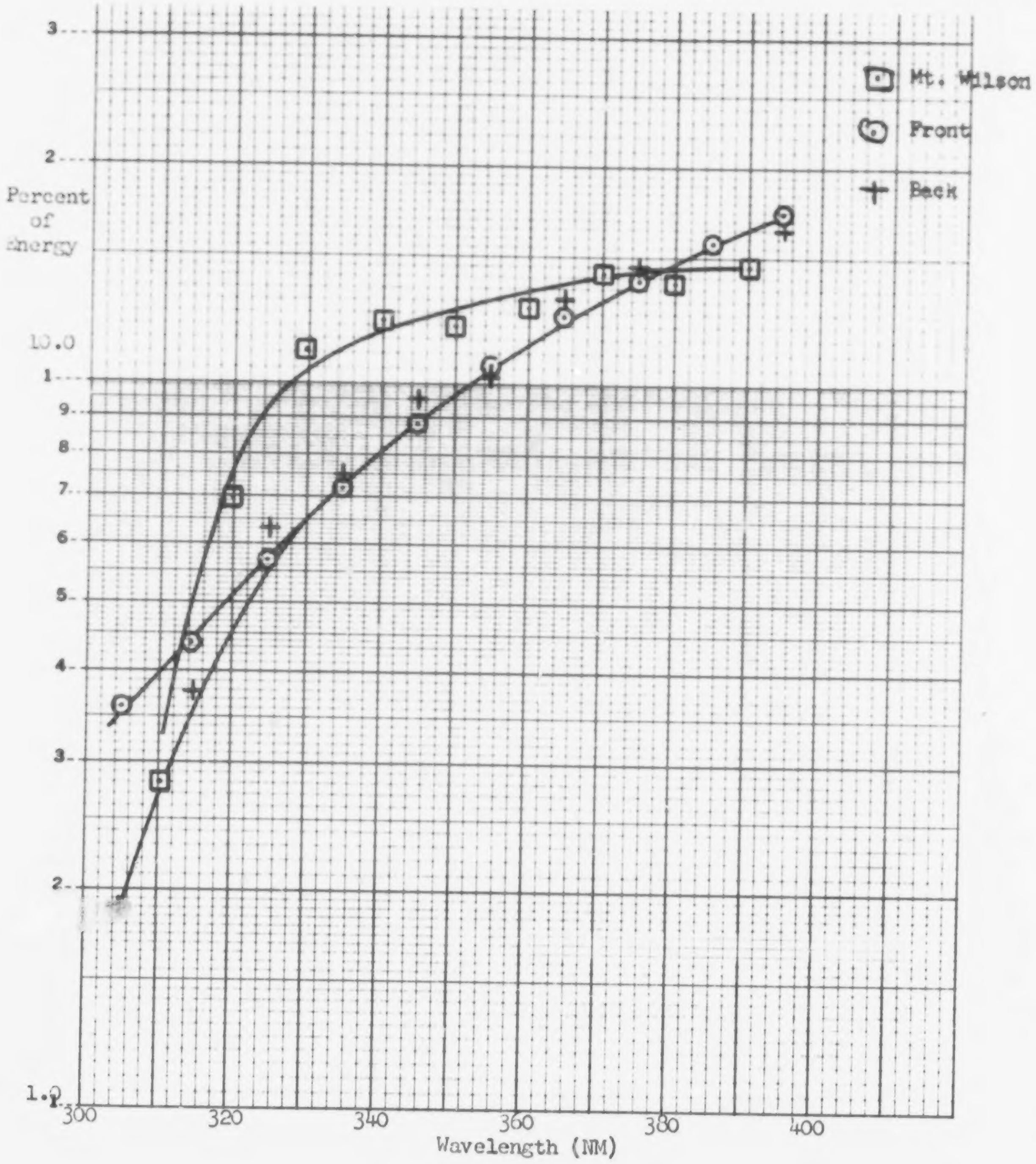

Fig. 4-20 Energy Distribution

5. PHOTOCHEMICAL EXPERIMENTS

The photochemical reaction runs were conducted as a series of replicates of the propylene-NO_x system starting at the same concentrations. Before each run, the chamber was cleaned by a vacuum technique. The reactants and products of interest were monitored on a continuous or periodic basis during the run. Detailed hydrocarbon analyses were conducted of samples obtained before and after each run. Data obtained was analyzed and the parameters of interest calculated.

5.1 Test Sequence

The smog chamber is detached from the charging and sampling manifolds. Water in the pressure relief valve is drained. The three-inch diameter cleanout port is opened. The smog chamber is then transferred to the vacuum chamber. The vacuum chamber is pumped down, subjecting the smog chamber internal and external surfaces to a pressure of 1-2 microns of Hg (10^{-3} torr). Offgassing at this pressure is continued for 15 to 30 hours with the chamber at 75°-85°F. The smog chamber is then repressurized with humidified ultra-zero air, while the vacuum chamber is re-pressurized with room air. During this operation, excess ultra-zero air is purged into the smog chamber and vents through the open cleanout port and pressure relief valve. A flow indicator is mounted in the cleanout port and observed to assure positive outflow throughout repressurization.

After repressurization, the vacuum chamber is entered and the cleanout port sealing plate reinstalled and the water seal refilled to seal the smog chamber from ambient air.

The smog chamber is then transferred to its irradiation station inside the thermal enclosure. The transfer takes about 5 minutes. Manifolds are reattached and a slow purge established with ultra-zero air to maintain the smog chamber at about 0.1 inch water pressure. Initial samples for total hydrocarbon analysis are then taken. This repressurization operation usually takes place the afternoon before the run.

On the day of the run, the total hydrocarbon content of the chamber is determined. Thermal enclosure heaters and fan are turned on to allow the smog chamber to come to thermal equilibrium. The side stream mixer is turned on.

Static calibration of the NO and NO_2 instruments is performed and baseline obtained. Instrument zero and calibration checks are performed on the GC instrumentation. After the chamber contents parameters are determined to be within the established criteria, charging the chamber with NO is initiated. When the NO concentration is suitable, gas samples are taken for individual hydrocarbon analysis and then propylene is charged. At least 40 minutes is allowed for propylene mixing. During this time, the illumination is turned on and allowed to stabilize with a shutter between the chamber and the light.

At time zero, the shutter is removed and chamber contents grab sampling initiated. Table 5-1 shows the chamber monitoring measurements taken; Table 5-2 shows the chemical analysis; and Table 5-3 gives a typical sample schedule. The chemical analyses are performed immediately after the sample is taken except for the formaldehyde bubblers (which are stored in the refrigerator and analyzed the next day); and the individual hydrocarbon analysis which is done the next day.

During the run, ultra zero air is added to the chamber to make up for sampling and leakage losses. Addition is through a wet test meter. Chamber pressure is maintained nominally at 0.1 inch water, during the run. Illuminator voltage and amperage is monitored and adjusted as needed to maintain constant power. The uv intensity meter is periodically monitored.

After the 300 minutes of illumination, post-test samples are taken. These include 1 or 4.4 liter gas samples used for individual hydrocarbon analysis; an IR cell sample; and a 6 liter concentration sample taken in a liquid nitrogen trap. The illuminator is then shut off. The chamber is purged after the run with bottled commercial air that has been through a charcoal absorber. This is continued for several hours, with the chamber at 100 to 105°F.

5.2 Test Conditions

Chamber conditions for the photochemical experiments are specified as 95 ± 3°F temperature at 25 ± 5% relative humidity (54 ± 5°F dew point). The initial air purity is specified as less than 0.1 ppm of ethylene, propylene, and butenes. The chamber charge is to consist of 3 ppm of propylene and 1.5 ppm of NO_x.

TABLE 5-1

CHAMBER MONITORING MEASUREMENTS

Measurement	Frequency
Chamber Pressure	10 minutes
Chamber Temperature	Continuous
Thermal Enclosure Temperature	10 minutes
Makeup Gas Quantity	10 minutes
Illumination Voltage/Amperage	10 minutes
UV Meter Reading	2 minutes

TABLE 5-2

CHAMBER CONTENTS CHEMICAL ANALYSIS

Pre-Run Measurements - Total Hydrocarbons and Detailed Hydrocarbons

Run Measurements	Frequency
NO_x	Continuous
NO_2	Continuous
Oxidant	Continuous
Propylene	10 minutes, then 15 and 20 minutes
Carbon Monoxide	30 minutes
Acetaldehyde	30 minutes
PAN	30 minutes
Formaldehyde	40 minutes
Oxidant by Manual Bubbler	40 minutes
Relative Humidity	60 minutes

Post-Run Measurements

- Detailed Hydrocarbons
- Cold Trapped Sample
- IR Cell Sample

TABLE 5-3
TYPICAL SMOG CHAMBER SAMPLE PLAN

Sample No.	Run Time (min.)	Propylene	CO	Acetaldehyde	PAN	Formaldehyde Bubbler	Oxidant Bubbler
1, A	-20	X	X	X	X		
2	-10	X					
3	0	X	X				
4	10	X					
B	15			X	X		
5	20	X					
6	30	X	X				
7	40	X				X	
C	45			X	X		
8	50	X					
9	60	X	X				X
10	70	X					
D	75			X	X		
11	80	X				X	
12	90	X	X				
13	100	X					X
E	105			X	X		
14	115	X	X				
	120					X	
15	130	X					
F	135			X	X		
	140						X
16	145	X	X				
17	160	X				X	
G	165			X	X		
18	175	X	X				
	180						X
19	190	X					
H	195			X	X		
	200					X	
20	205	X	X				
21	220	X					
I	225			X	X		
22	240	X	X			X	
J	255			X	X		
23	260	X	X				
24	280	X	X			X	
K	285			X	X		
25, L	300	X	X	X	X		X

5.3 Test Results

Chamber behavior was consistent with that reported for other smog chambers. Propylene disappeared slowly at first, then at an increased rate as NO_2 built up, and then at a decreasing rate as the NO_2 decreased. NO_2 concentration rose and then fell to give a rather sharp peak. Oxidant started to build up as NO_2 started decreasing, reached a broad maximum and slowly drifted down. Acetaldehyde and formaldehyde started building up as propylene entered the rapid disappearance region. PAN started appearing after oxidant peaked. Carbon monoxide increased steadily during the run.

Cumulative gas addition to the chamber was 275, 306, and 350 liters, respectively, which gave a range of 13.7 to 17.1% dilution over the 5-hour runs, based on the well stirred flow reactor approximation.

The chamber temperature profile with time was consistent for the three runs. The temperature at time zero was 83, 82, and 82°F. The temperature was at 92°F in about 40 minutes, and rose to 95°F about 2 hours into the runs. The end of run temperature was 97, 95, and 95°F respectively. Temperature rises during the run because the gas absorbs energy from the light beam. Chamber relative humidity varied slowly from 25% to 29% (55 to 58°F dew point) for all three runs.

Illumination power was held constant at 6700 watt during the runs. The beam intensity monitor showed constant power during the runs.

Concentration plots are shown in Figures 5-1 to 5-9 for the species discussed. Table 5-4 gives the calculated chamber results such as dosages and half times which are defined as given below, in conformance with the definitions used by CRC CAPI-6 Project.

Initial Concentration:

HC = Hydrocarbon
$NO_x = NO + NO_2$
$NO_2 = NO_2$

NO_2 Formation:

Rate = $\frac{NO_i}{2T_{\frac{1}{2}}}$ where $T_{\frac{1}{2}}$ is the time to form an amount of NO_2 equal to ½ the initial NO in addition to the NO_2 present initially; and NO_i is the initial NO concentration in ppb.

T_{max} = time, in minutes, to the maximum NO_2 concentration

Dose = $\int_0^{300} [NO_2]\, dt$ where $[NO_2]$ is NO_2 and t = minutes.

Oxidant Formation:

Max. Rate = $\frac{\text{Max. Oxidant}}{2(T_{3/4} - T_{1/4})}$ where $T_{3/4}$ and $T_{1/4}$ are the times, in minutes to form 3/4 and 1/4 the maximum oxidant; and Max. Oxidant is the maximum oxidant concentration in ppb.

Avg. Rate = $\frac{\text{Max. Oxidant}}{2T_{\frac{1}{2}}}$ where $T_{\frac{1}{2}}$ is the time, in minutes, to form ½ the maximum oxidant, and Max. Oxidant is the maximum oxidant concentration in ppb.

Max. Conc. = maximum oxidant concentration in ppm

$T_{max.}$ = time, in minutes, to the maximum oxident concentration

Dose = $\int_0^{300} (\text{Oxidant})\, dt$ where Oxid. is oxidant and t = minutes.

Hydrocarbon Disappearance:

Final Conc. = ppm hydrocarbon after 300 minutes irradiation

$T_{0.75}$, $T_{0.5}$ & $T_{0.25}$ = are the times, in minutes, required to reduce the hydrocarbon concentration to 3/4, 1/2, and 1/4 of the original concentration.

Max. Rate = $\frac{HC_i - HC_f}{2(T_{3/4} - T_{1/4})}$ where $T_{3/4}$ and $T_{1/4}$ are times, in minutes, for the disappearance of 3/4 and 1/4, respectively, of the hydrocarbon disappearing in 300 minutes; HC_i is the initial hydrocarbon concentration in ppb; and HC_f is the final hydrocarbon concentration in ppb.

Avg. Rate = $\frac{HC_i - HC_f}{2T_{\frac{1}{2}}}$ where $T_{\frac{1}{2}}$ is time, in minutes, for the disappearance of ½ the hydrocarbon disappearing in 300 minutes; HC_i is the initial hydrocarbon concentration in ppb; and HC_f is the final hydrocarbon concentration in ppb.

Max. Ald. = Maximum total aldehyde concentration in ppm as formaldehyde.

Max. PAN = Maximum peroxyacetylnitrate concentration in ppm.

TABLE 5-4

CHAMBER RESULTS - PROPYLENE

	Initial Conc. (ppm)			NO_2 Formation			Oxidant Formation				
	HC	NO_x	NO_2	Rate (ppb/min)	T_{max} (min)	Dose (ppm-min)	Max Rate (ppb/min)	Avg Rate (ppb/min)	Max Conc. (ppm)	T_{max} (min)	Dose (ppm-min)
Run 1	3.00	1.63	0.20	16	67	171	9.5	3.7	0.61	125	98
Run 2	2.62	1.54	0.15	14	98	186	13	2.6	0.56	150	86
Run 3	2.85	1.45	0.09	15	80	123	12	3.1	0.50	115	82

	Hydrocarbon Disappearance								
	Final Conc. (ppm)	$T_{0.75}$ (min)	$T_{0.5}$ (min)	$T_{0.25}$ (min)	Max Rate (ppb/min)	Avg. Rate (ppb/min)	Max Formald (ppm)	Max PAN (ppm)	Max Acetald. (ppm)
Run 1	0.06	64	88	108	33	17	0.90	0.44	1.0
Run 2	0.03	75	113	138	24	11	1.2	0.55	1.4
Run 3	0.03	73	94	122	29	15	1.3	0.38	.88

Notes: Chamber Conditions:

Temperature 95°F

Relative Humidity 25%

K_d 0.35 min^{-1}

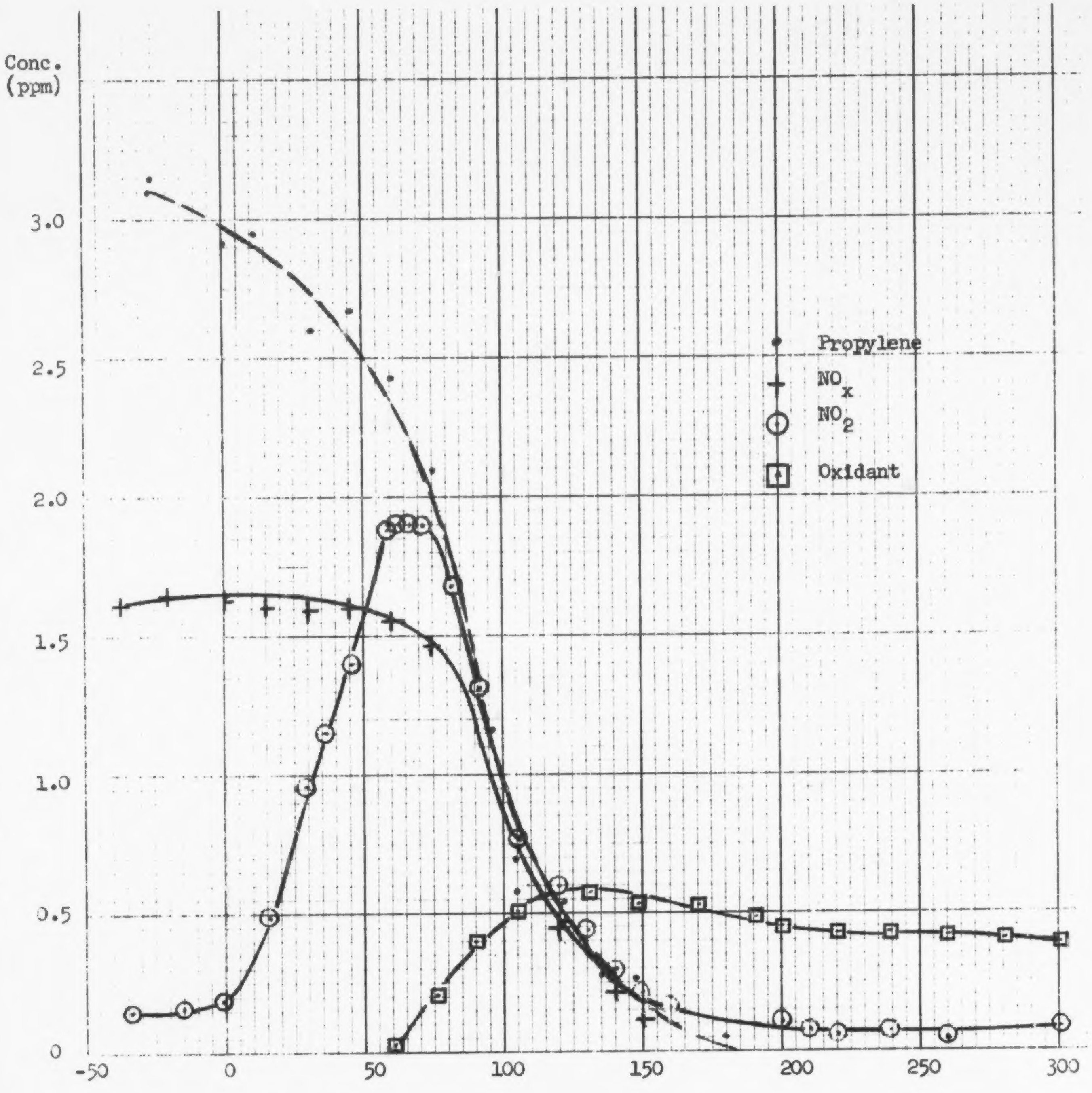

Fig. 5-1 Run 1 Propylene, NO_x, NO_2 and Oxidant

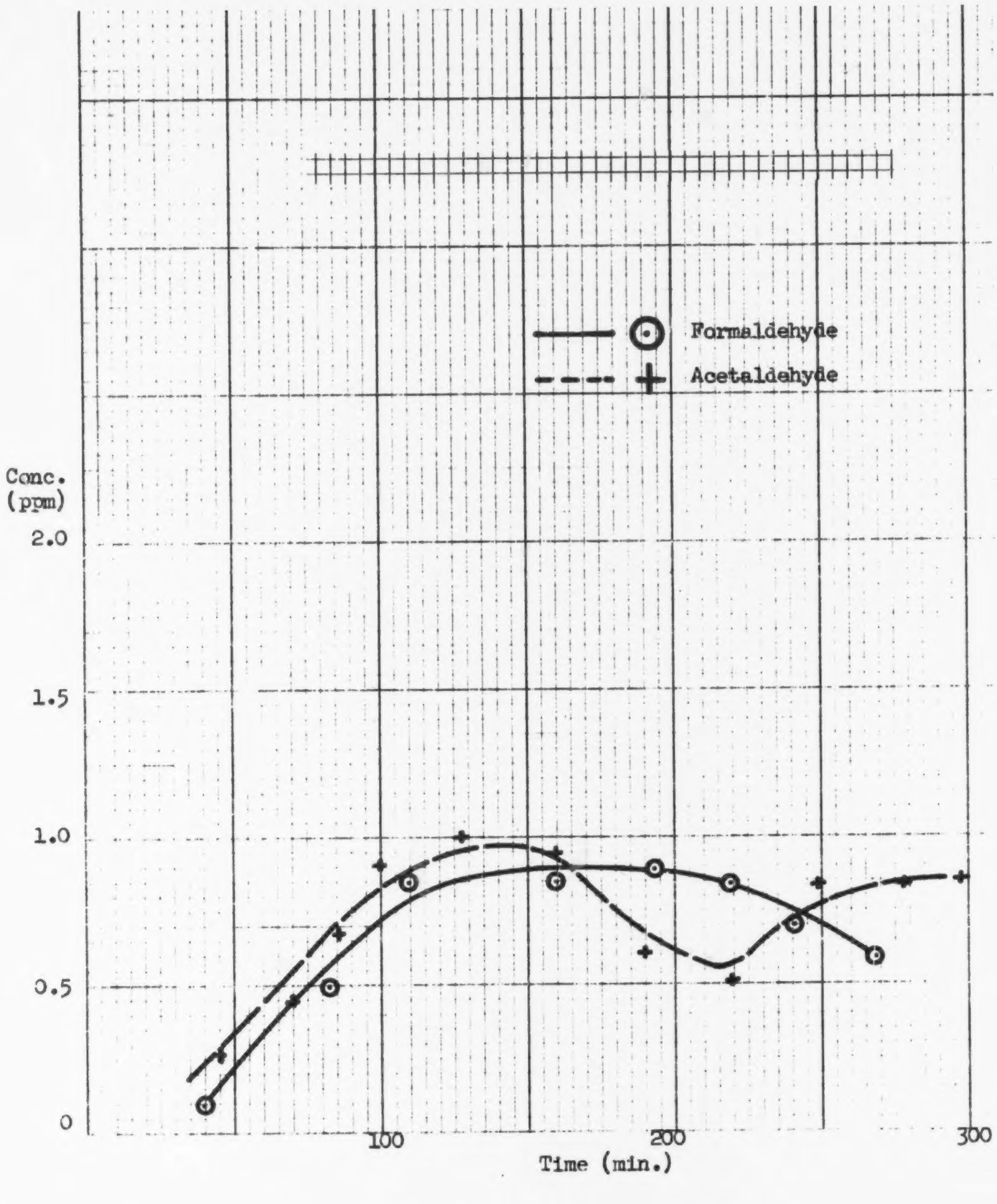

Fig. 5-2 Run 1, Formaldehyde and Acetaldehyde

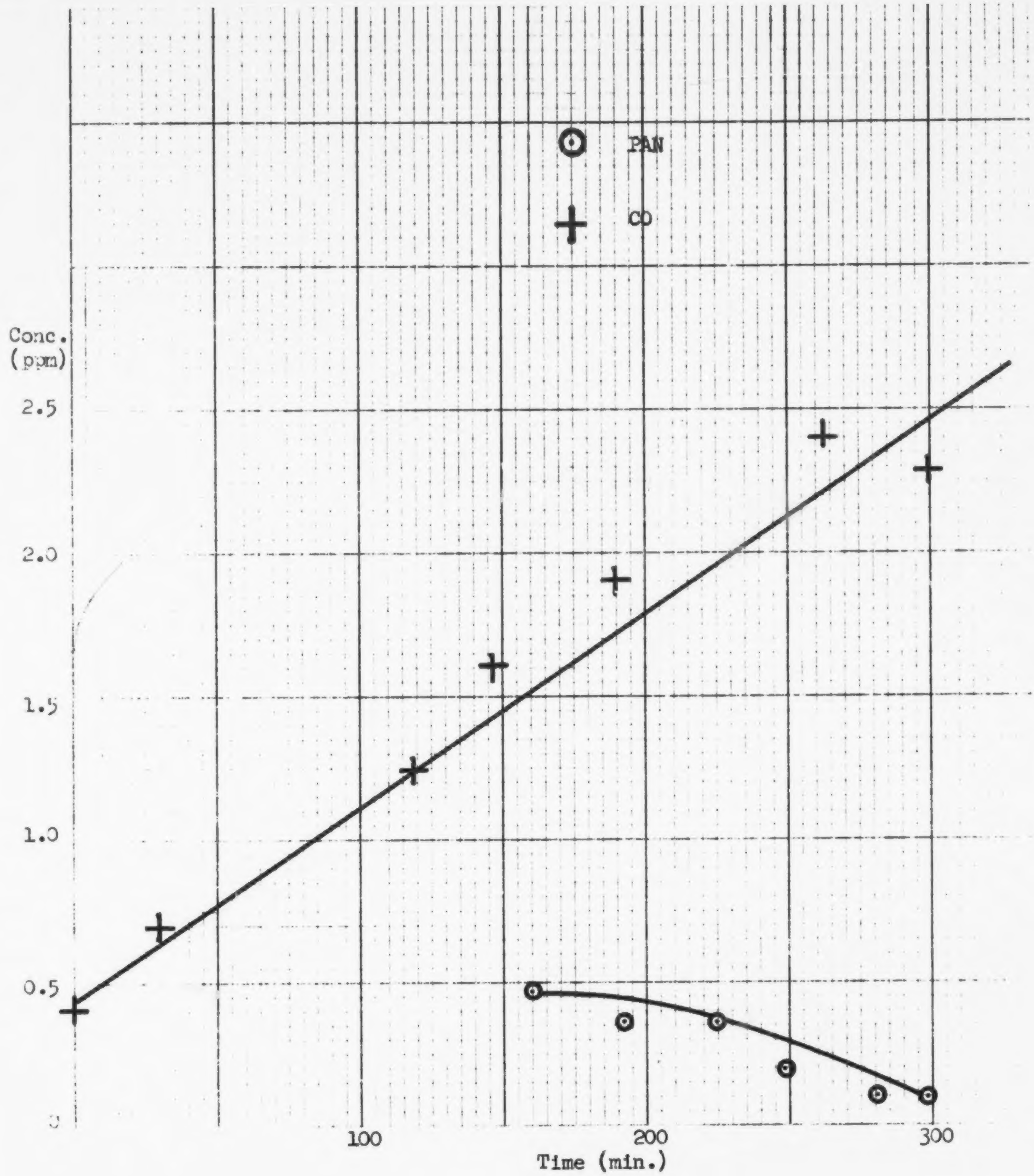

Fig. 5-3 Run 1 PAN and CO

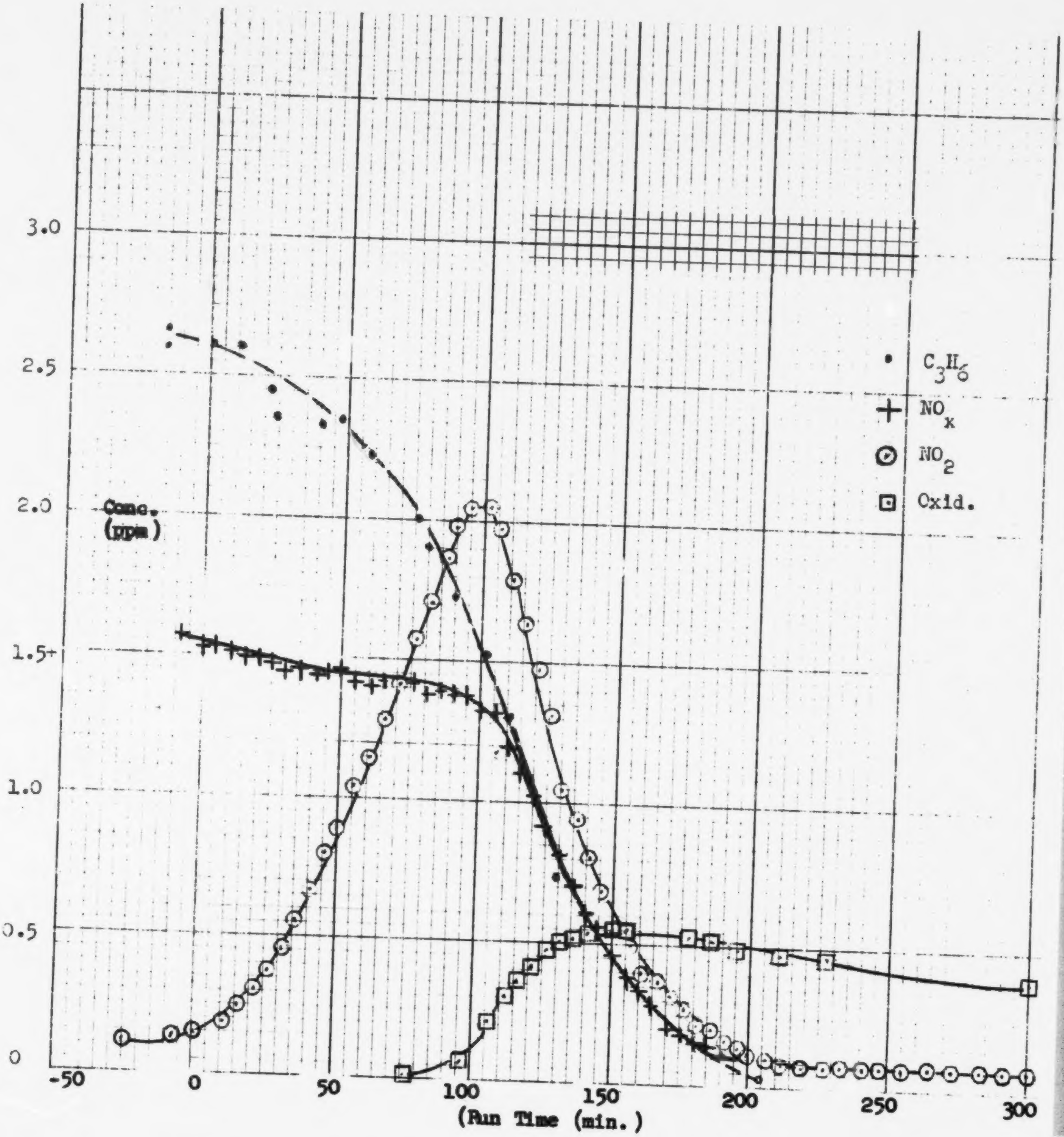

Fig. 5-4 Run 2, Propylene, NO_x, NO_2, Oxidant

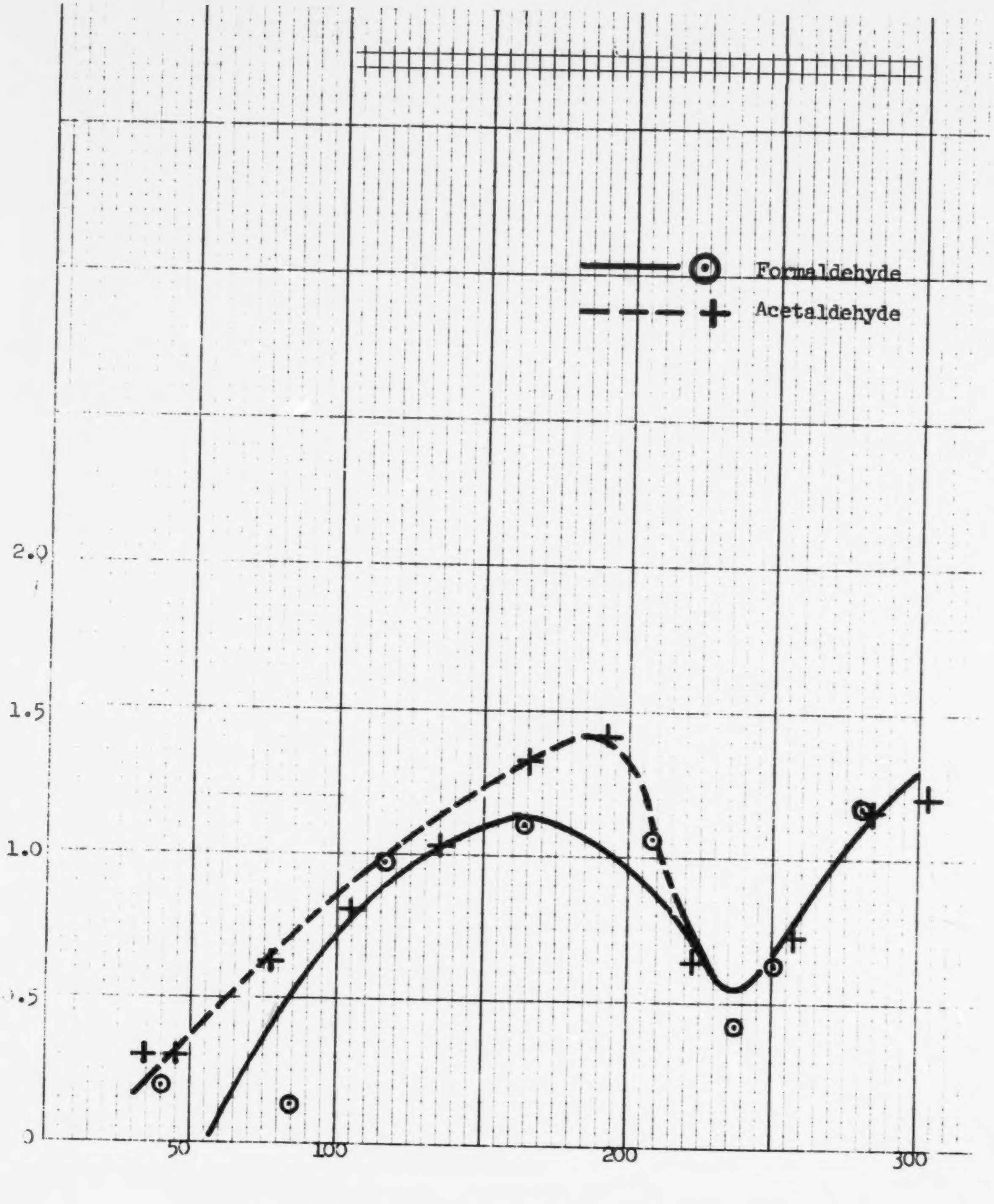

Fig. 5-5 Run 2, Formaldehyde and Acetaldehyde

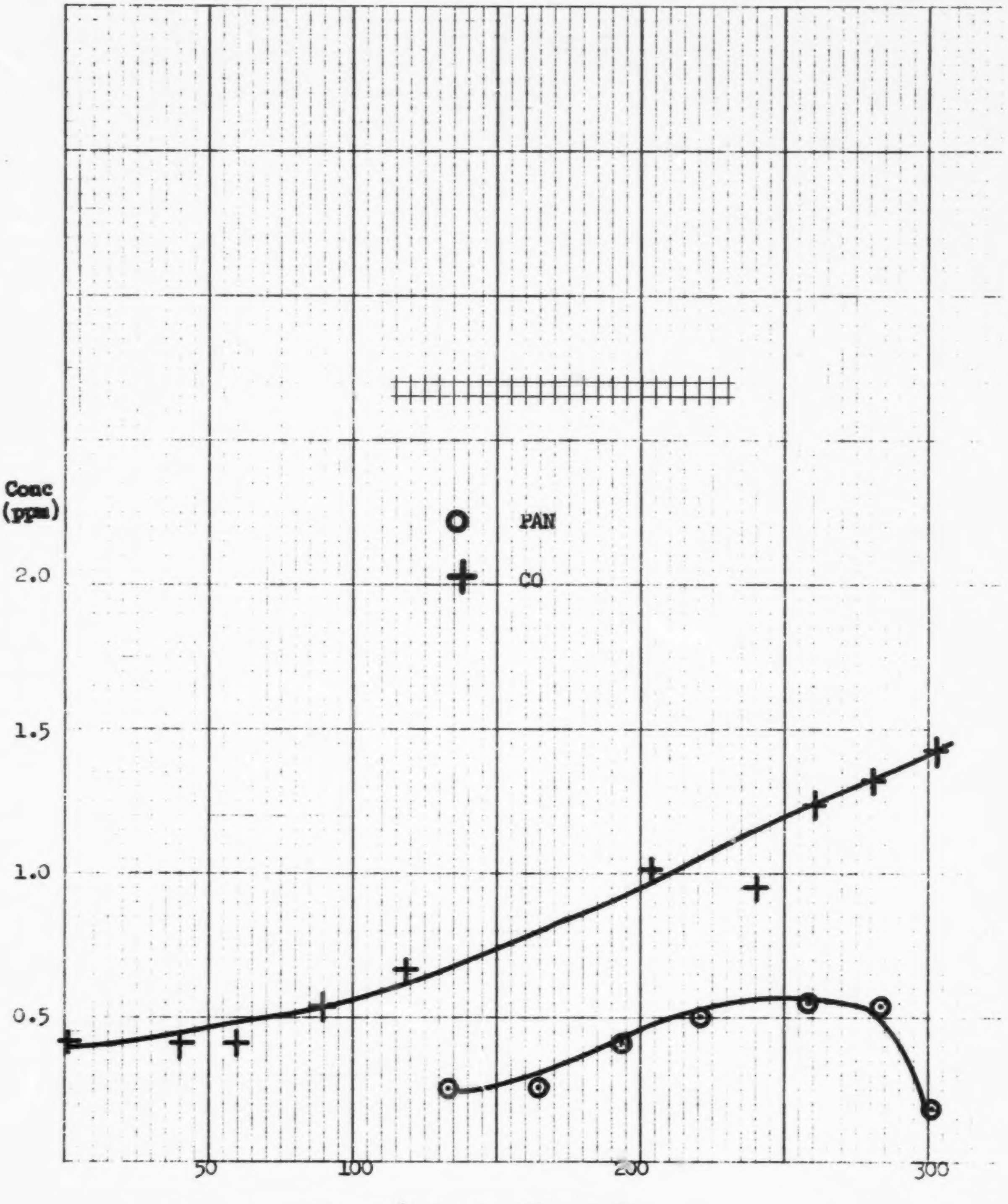

Fig. 5-6 Run 2 PAN and CO

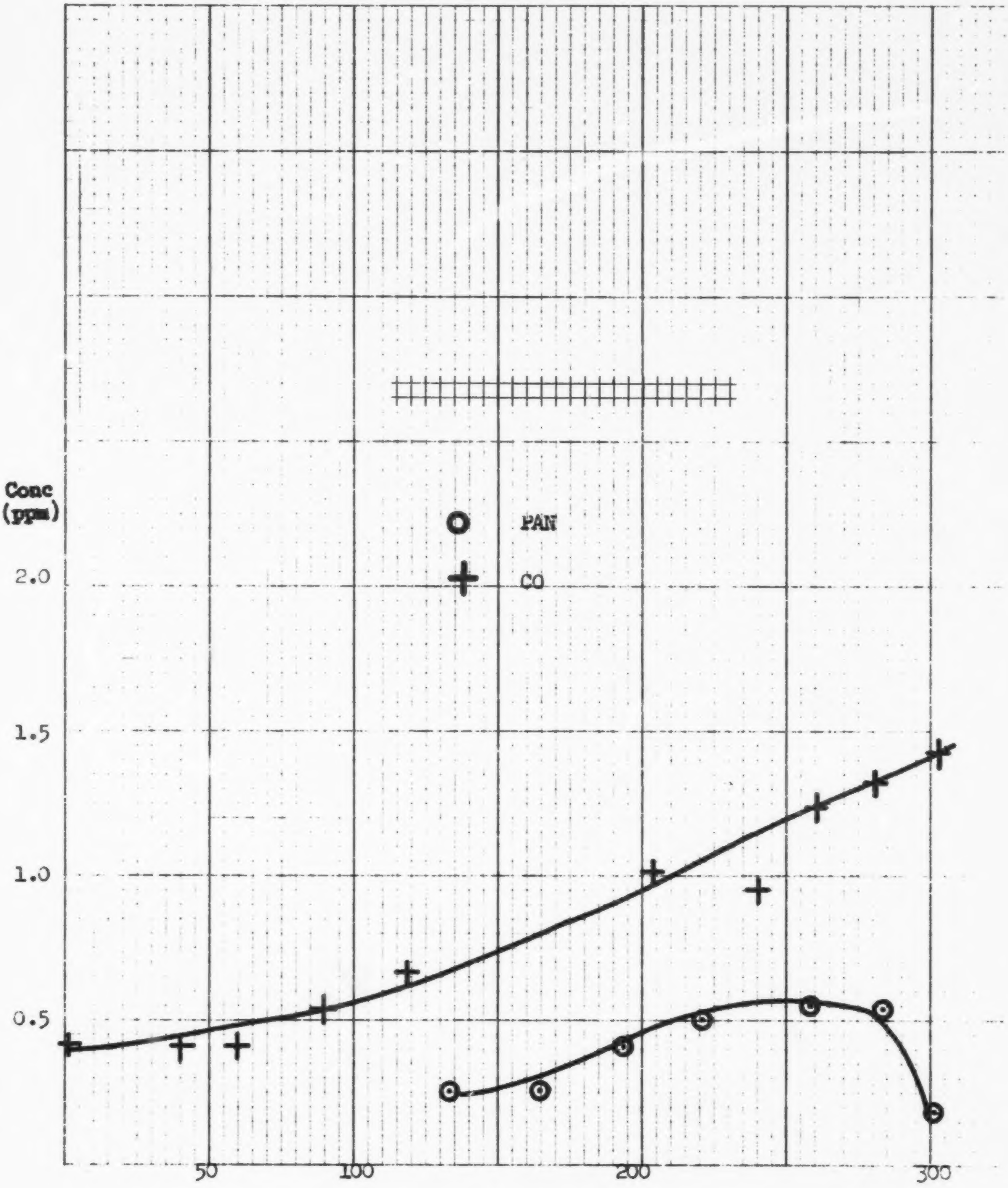

Fig. 5-6 Run 2 PAN and CO

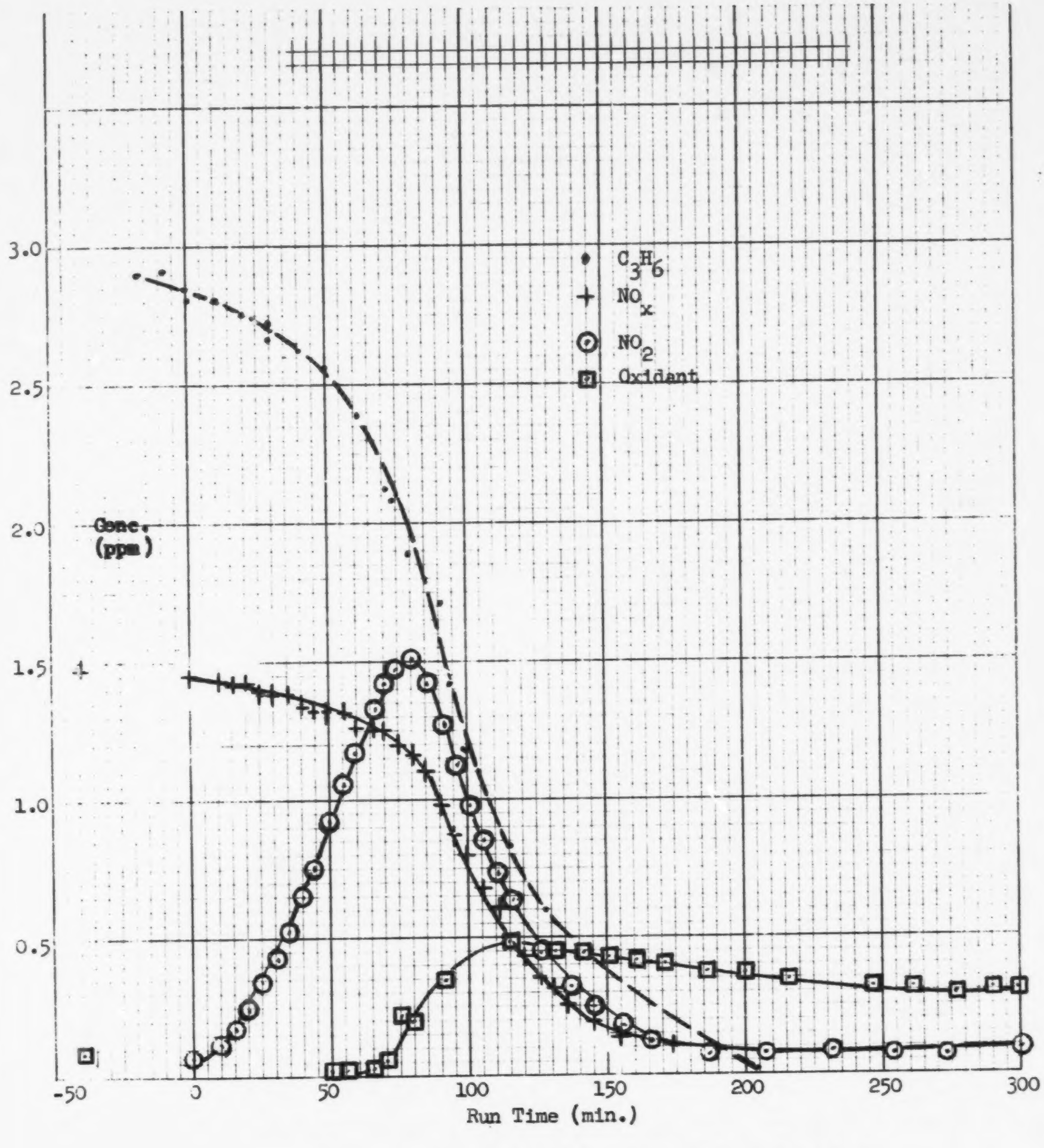

Fig. 5-7 Run 3, Propylene, NO_x, NO_2 and Oxidant

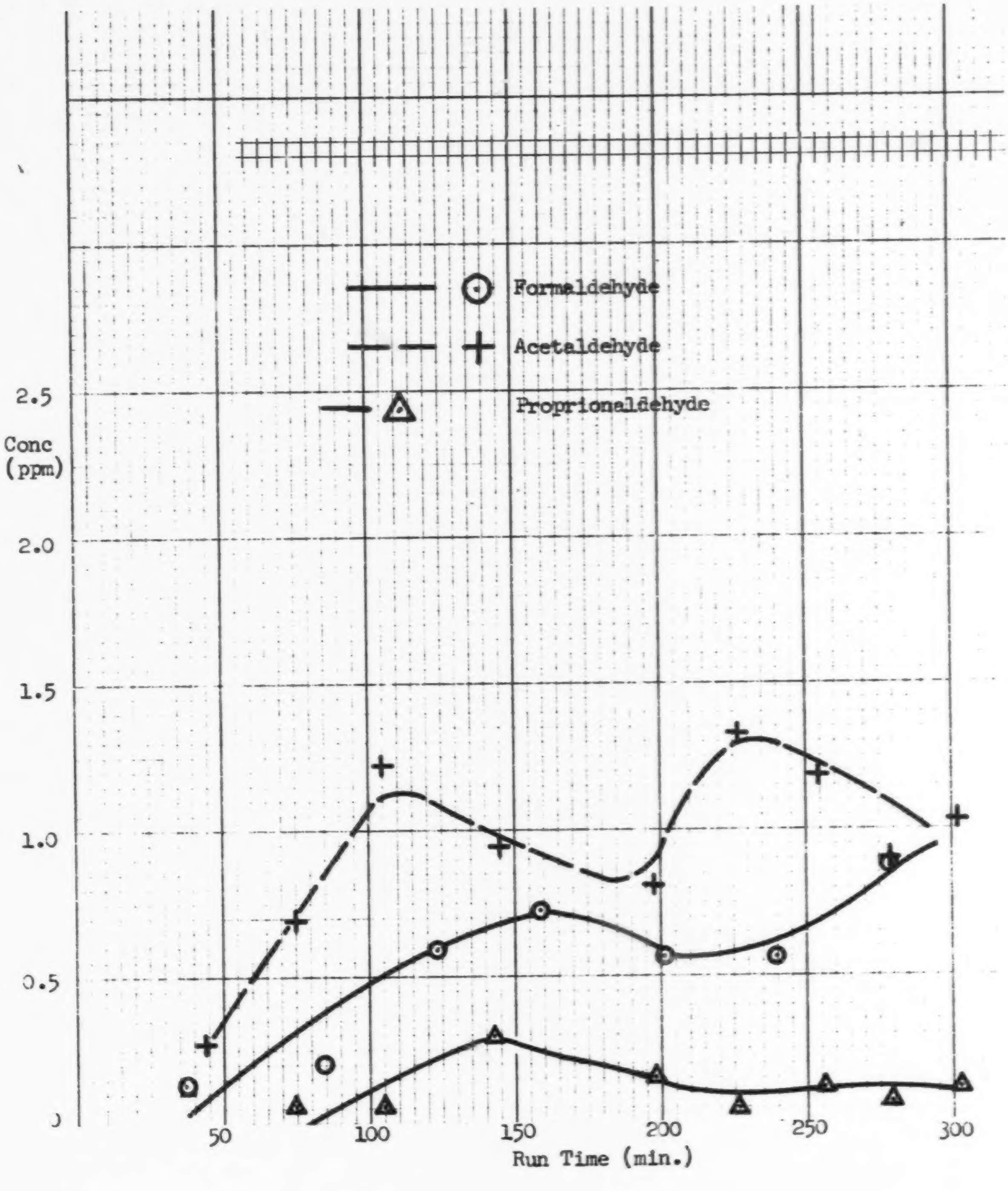

Fig. 5-8 Run 3, Formaldehyde, Acetaldehyde and Proprionaldehyde

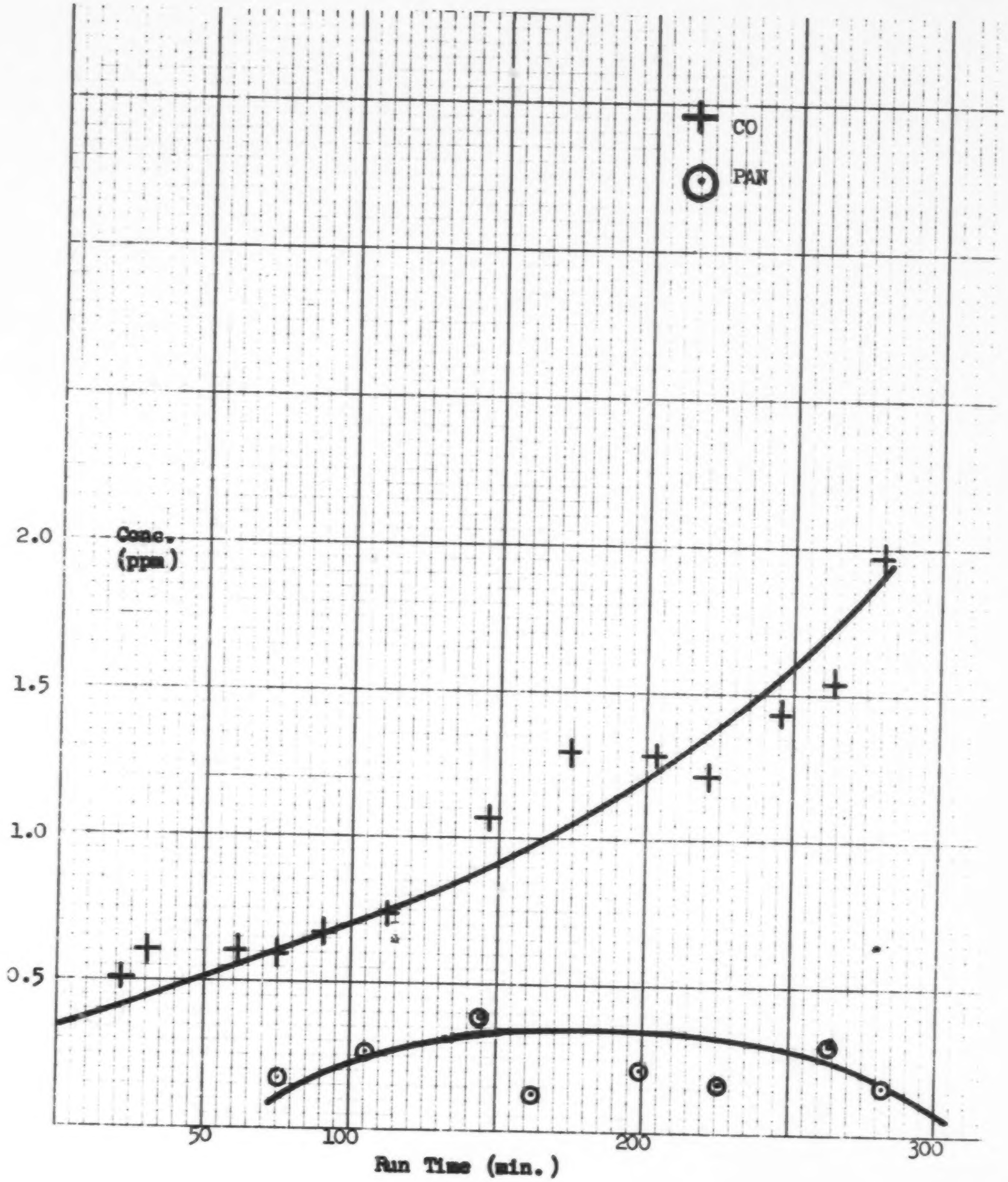

Fig. 5-9 Run 3, PAN and CO

5.4 Results Discussion

Average values for the chamber results are given in Table 5-5, along with the standard deviation. These deviations agree favorably with similar deviations calculated, based on the CAPI-6 reproducibility runs that were made available to LMSC. The CAPI data is based on five replications, and thus is considered more representative than the three-replications data.

5.4.1 Oxidant Analysis

Oxidant was analyzed using both the Mast oxidant meter and by manual bubbling of the chamber gas through 2% neutral KI solution. The solution composition for both instruments is identical. Table 5-6 shows the comparison between the bubbler and the Mast readout, without corrections for NO_2 or PAN interference. The agreement is good, and as the Mast data is continuous, it is used. The oxidant data is corrected for NO_2 response by a factor of 15 (Section 3.).

5.4.2 NO_2 and NO_x Analysis

Pre-run calibrations were conducted for the NO_2 and NO_x instrumentation. Prior to each smog chamber run, a static calibration using $NaNO_2$ solutions from 0.02 to 2 ppm NO_2 was run. Usually four points were run, although for the 1st and 3rd photochemical runs, an eight-point static calibration curve was established. Before the dummy run and the second photochemical run, dynamic calibrations for NO_2 and NO similar to that described in Section III were run. Oxidizing columns were preconditioned by passing air through them overnight. No significant variations in the dynamic calibrations were noted, indicating constant oxidizing tube efficiency. The instrument flowmeters were calibrated with a wet test meter at 100, 150, and 200 cc/min sampling rates and were set and checked at 150 cc/min. The liquid flow rate was checked before every run, as the tubes on the Technicon and Beckman pumps were changed prior to each run.

The peak NO_2 concentration for all three runs exceeded the initial NO_x concentration:

TABLE 5-5

CHAMBER RESULTS SUMMARY

PROPYLENE/NO_x SYSTEM

3/1.5 ppm

NO_2 Formation	Average	Sample Std. Deviation
Rate, ppb/min	15	1.0
T max, min	82	15.6
Dose, ppm x min	160	33.
Oxidant Formation		
Max. Rate, ppb/min	11.5	1.8
Avg. Rate, ppb/min	3.1	0.55
Max. Conc, ppm	0.56	0.053
T max, min.	130	15
Dose, ppm x min	89	8.6
Hydrocarbon Disappearance		
T 0.75, min.	71	5.9
T 0.50, min.	98	13.2
T 0.25, min.	123	15
Max Rate, ppb/min	29	4.6
Avg. Rate, ppb/min	14	3.1
Max Formaldehyde, ppm	1.1	0.21
Max PAN, ppm	0.46	0.087
Max. Acetaldehyde, ppm	1.1	0.28

TABLE 5-6

COMPARISON OF OXIDANT CONCENTRATIONS*

Run No.	Run Time (min)	Mast Reading (ppm)	Colorimetric Result (ppm)
Run 1	74	0.33	0.40
	140	0.59	0.64
	180	0.54	0.60
	300	0.42	0.57
Run 2	60	0.08	0.08
	100	0.20	0.12
	140	0.54	0.36
	180	0.54	0.50
	300	0.38	0.38
Run 3	58	0.09	0.05
	104	0.47	0.48
	141	0.49	0.45
	173	0.40	0.40
	300	0.31	0.33

*Neither reading corrected for NO_2.

	Initial NO_x	Peak NO_2	Percentage "Excess" NO_2
Run 1	1.63	1.92	17.5
Run 2	1.54	2.16	40
Run 3	1.48	1.53	3.5

Possible explanations for this observation have been sought in the monitoring technique, the instrumentation, and in physical behavior of NO and NO_2 but no satisfactory explanation has been found.

Saltzman's original article on the NO_2 analysis method (Ref. 5-1) was consulted. No interference was found from nitric acid vapors, or liquid nitric acid solution, and probably none from N_2O_5 (10% response indicated but may be caused by NO_2). In further studies of the original reagent, Thomas (Ref. 5-2) observed a mole-for-mole response from ethyl nitrite and about a 50% response from butyl and amyl nitrites.

At this point, no satisfactory explanation can be offered for the observed data. It is planned to conduct further testing using a chemilumenscent NO monitor in conjunction with Saltzman technique monitoring of NO_2. It is understood that similar data has been observed on at least some occasions at other smog chambers.

5.4.3 Results for Aldehydes

Figures 5-2, 5-5, and 5-8 show the results obtained for formaldehyde and acetaldehyde. As previously noted in the literature for the propylene/NO_x photochemical system (Ref. 3-5), these products appear early in the run, and show similar yields. The time pattern described in Ref. 5-3 is for the aldehyde to reach a maximum or level off, and then decrease after almost all the propylene and at least 90% of the nitrogen oxide is consumed. These features were noted in the results. In addition, a second increase in aldehyde concentration was noted for five of the six possible occurrences.

This behavior has not been previously reported, to our knowledge. As it was observed using two independent monitoring techniques (a gas bulb sample and subsequent GC determination for acetaldehyde, and a direct gas sample through chromotropic acid solution and subsequent colorimetry for formaldehyde), the second increase is believed to be real. No attempt has been made to formulate a mechanism.

The acetaldehyde GC column is also sensitive to organic acids and keto structures. For Run 3, identification of **propionaldehyde** was possible based on GC retention time. The **propionaldehyde** appears at about 1/10th the concentration of acetaldehyde. There are indications that acetic acid is present, and possibly also formic acid and methyl ethyl ketone.

5.4.4 Analysis of Individual Hydrocarbon Samples and Minor Products Identification

The pre-run samples were concentrated using a liquid nitrogen trap and the detailed hydrocarbon analysis conducted as outlined in Section 3. No unsaturated hydrocarbons of C_6 or below were detected. The lower limit of detectability for this technique is estimated at 0.01 ppm. For Run 1, some six small peaks were seen at estimated concentration levels of about 0.05 ppm. Tentative identification is **propionaldehyde**, n-propyl alcohol, methyl ethyl ketone, and possibly n-hexane and a benzene derivative. The Run 2 pre-run sample showed acetaldehyde at about 0.05 ppm, acetic acid at about 0.02 ppm, and three other components that may include **propionaldehyde**, methyl ethyl ketone, and a benzene derivative.

For run 3, a longer period of vacuum chamber off-gassing was used at a lower pressure (0.8 microns) than was possible for the Runs No. 1 and 2 vacuum treatments (1.7 and 2.8 microns respectively). In addition, the sampling manifolds were subjected to a separate 2-hour purge with ultra-zero nitrogen. The Run 3 pre-run concentration sample showed one unidentified peak for one sample, and no peaks for a second sample.

The post-test detailed hydrocarbon samples showed acetaldehyde at about 0.3 ppm, and for Runs 1 and 3 propylene at about 0.05 ppm, and for Runs 2 and 3, an unidentified high boiling compound that elutes from the column at about 180°C and may be the same benzene derivative identified in the pre-run samples.

The report presents results ~~[illegible]~~ of factors affecting environmental chambers used to study photochemical reactions in the lower atmosphere. Discussed are the facilities, ~~analytical methodology~~, the chambers, the light source, and some photolysis [illegible]

6. CONCLUSIONS AND RECOMMENDATIONS

The work conducted under this contract has shown the practicality of operating an environmental chamber externally illuminated by a collimated beam of light from an xenon arc lamp. It has also demonstrated that a vacuum chamber pumpdown of the environmental chamber is a feasible method of chamber cleaning. Analytical chemistry methodology has been demonstrated for the photochemical reaction products of interest.

It is recommended that additional work to further the objectives of the CAPA-I-69 project be undertaken, to elucidate the importance of the following factors affecting reactions in environmental chambers:

- Surface to Volume Ratio for the reference Pyrex material
- Use of aluminum, stainless steel, and fluorocarbon film as environmental chamber materials, at various S/V ratios
- Variation in spectral distribution of the illumination to show the importance of various wave-length regions, such as the 300 to 320 nm interval
- Variation in intensity-time relationship of the radiation
- Variations in radiation intensity
- Cleaning techniques for environmental chambers.

This work should be preceded by a more complete set of experiments on the basic configuration chamber, which would include background reactivity measurements, repeat ozone halflife measurements, and additional photochemical experiments on the propylene/NO_x system.

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REFERENCES

1-1 D.B. Wimmer, Factors Affecting Reactions in Environmental Chambers, Coordinating Research Council, Air Pollution Research Advisory Committee, May 1971.

2-1 D. E. Grey (ed), American Institute of Physics Handbook, 2nd.ed., McGraw-Hill, 1963, p. 6-119.

3-1 N. A. Lyshkow, "A Rapid and Sensitive Colorimetric Reagent for Nitrogen Dioxide in Air", J. Air Poll. Control Assoc., 15, 481 (1965).

3-2 Technicon Air Pollution Control Detection Systems Instruction Manual 7-67-105, Technicon Corporation, Ardsley, New York.

3-3 Metronics Associates, Inc., Technical Bulletins No. I-68 and 20-68.

3-4 Air and Industrial Hygiene Laboratory, State of California, Department of Public Health, Tentative Recommended Method No. 2A, "Analysis for Total Oxidant Content of the Atmosphere", 1969.

3-5 A. P. Altshuller, S. L. Kopczinski, et al, Environ. Sci. & Tech., 1, 899 (1967).

3-6 B. Dimitriades, J. Air Pollution Cont. Assoc., 17, 460, (1967).

3-7 A. P. Altshuller, et al., Anal. Chem., 33, 621 (1961).

3-8 J. N. Cares, Amer. Ind. Hyg. Assoc., 29, 405 (1968).

3-9 Bay Area Air Pollution Control District, Method F-1, 1971.

3-10 E. R. Stephens, "Production of Peroxyacetyl Nitrate (PAN) Samples for Instrument Calibration", Statewide Air Pollution Research Center, University of California, Riverside.

3-11 E. H. Kawasaki, et al., Catalog of Infrared and Mass Spectra and Gas Chromatographic Retention Time Indices of Trace Contaminants, LMSC 672406, 24 Jan. 1967, Lockheed Missiles & Space Co.

4-1 C. S. Tuesday, Photo-Oxidation of t-Butene-2 and Nitric Oxide in Chemical Reactions in the Lower and Upper Atmosphere, Interscience Publ. 1961.

4-2 A. P. Altshuller and J. J. Bufalini, Environ. Sci. & Tech., 5, 38, (1971).

4-3 R. J. Gordon, Photochemical Measurements in Pilot Study of Ultraviolet Radiation in Los Angeles, Oct. 1965, Nat. Air Pollution Control Admin., Pub. 999-AP-38.

4-4 H. S. Johnston, Project Clean Air, Task Force Assessment, Vol. 4, University of California (1970).

4-5 J. S. Nader, Filter-Photocell Measurement in Pilot Study of Ultraviolet Radiation in Los Angeles, Oct. 1965, Nat. Air Pollution Control Admin., Pub. 999-AP-38.

5-1 B. E. Saltzman, Anal. Chem., 26, 1949 (1954).

5-2 M. D. Thomas et al, Anal. Chem., 28, 1810 (1956).

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